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MATHEMATIK

EIN MINIMALPROBLEM IN DER THEORIE DER MOMENTFOLGEN UND DIE ABSCHÄTZUNG DER POLYNOME. II

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(Vorgelegt von S. N. Bernstein, Mitglied der Akademie, d. 25. V. 1936)

Im ersten Teil unserer Arbeit (1) wurde die Existenz der Grösse N_{μ_n} bewiesen, die die Abschätzung aller symbolischen Polynome $P_n(\mu)$ angibt, nämlich:

$$|P_n(\bar{\mu})| \leqslant N_{\mu_n} \cdot \max_{(0,1)} |P_n(x)|$$

und dabei $N_{\mu_n} \leqslant M_{\min}$ ist.

Hier beweisen wir zunächst, dass $N_{\mu n} = M_{\min}$ ist.

Satz 1. *Ist die Folge der Grössen* $\mu_0, \mu_1, \ldots, \mu_n$ *angegeben, so kann man immer diese endliche Folge um eine Grösse* μ_{n+1} *so vermehren, dass die Abschätzung auch für die Menge* $\{P_{n+1}(x)\}$ *gültig bleibt, d. h.:* $N_{\mu_{n+1}} = N_{\mu_n}$ *oder*

$$|P_{n+1}(\bar{\mu})| \leqslant N_{\mu_n} \cdot \max |P_{n+1}(x)|.$$

Jedes Polynom, genau $(n+1)$-ten Grades kann eindeutig in der Form $P_{n+1}(x) = P_n(x) + \alpha x^{n+1}$ dargestellt werden, wobei $\alpha \neq 0$ ist.

Da die Menge $\left\{\frac{P_{n+1}(\mu)}{\max |P_n(x)|}\right\}$ bei beliebigem μ_{n+1}, von den Zahlen $\pm N_{\mu n+1}$ begrenzt ist, genügt es die rechte Grenze festzustellen. Für zwei beliebige Polynome n-ten Grades haben wir:

$$Q_n''(\bar{\mu}) - Q_n'(\bar{\mu}) = [Q_n''(x) - Q_n'(x)_\mu \leqslant N_{\mu_n} \cdot \max |Q_n''(x) - Q_n'(x)| =$$
$$= N_{\mu_n} \cdot \max |Q_n''(x) + x^{n+1} + [-Q_n'(x) - x^{n+1}]| \leqslant N_{\mu_n} \cdot \max |Q_n''(x) + x^{n+1}| +$$
$$+ N_{\mu_n} \cdot \max |Q_n'(x) + x^{n+1}|,$$

d. h.

$$-Q_n'(\bar{\mu}) - N_{\mu_n} \cdot \max |Q_n'(x) + x^{n+1}| \leqslant -Q_n''(\bar{\mu}) +$$
$$+ N_{\mu_n} \cdot \max |Q_n''(x) + x^{n+1}|. \qquad (1)$$

Die linke Seite dieser Ungleichung ist immer

$$\leqslant |Q_n'(\bar{\mu})| - N_{\mu_n} \cdot \max |Q_n'(x) + x^{n+1}| \leqslant N_{\mu_n} \cdot \max |Q_n'(x)| -$$
$$- N_{\mu_n} \cdot \max |Q_n'(x) + x^{n+1}| \leqslant N_{\mu_n} \cdot \max x^{n+1} = N_{\mu_n};$$

d. h. sie hat eine genaue obere Grenze m.

Die rechte Seite der Ungleichung (1) ist immer

$$\geqslant N_{\mu_n} \cdot \max |\, Q_n''(x) + x^{n+1} \,| - |\, Q_n''(\bar{\mu}) \,| \geqslant N_{\mu_n} \cdot \max |\, Q_n''(x) + x^{n+1} \,| - N_{\mu_n} \cdot \max |\, Q_n(x) \,| \geqslant N_{\mu_n};$$

hat also eine genaue untere Grenze M. Nach (1) ist $m \leqslant M$.

Nehmen wir μ_{n+1} als eine beliebige Zahl aus dem Intervalle $m \leqslant \mu_{n+1} \leqslant M$. Dann ist, falls $\alpha > 0$:

$$\alpha \cdot \mu_{n+1} \leqslant -P_n(\bar{\mu}) + N_{\mu_n} \cdot \max |\, P_n(x) + \alpha x^{n+1} \,|$$

oder $P_{n+1}(\bar{\mu}) \leqslant N_{\mu_n} \cdot \max |\, P_{n+1}(x) \,|$. Falls aber $\alpha < 0$ ist, so erhält man:

$$\alpha\, |\, \mu_{n+1} \leqslant -P_n(\bar{\mu}) + N_{\mu_n} \cdot \max \big|\, |\, \alpha \,| \cdot Q_n'(x) + |\, \alpha \,| \cdot x^{n+1} \,\big| = -P_n(\bar{\mu}) + N_{\mu_n} \cdot \max |\, P_n(x) + \alpha x^{n+1} \,|,$$

d. h.

$$P_{n+1}(\bar{\mu}) \leqslant N_{\mu_n} \cdot \max |\, P_{n+1}(x) \,|.$$

Also $|\, P_{n+1}(\bar{\mu}) \,| \leqslant N_{\mu_n} \cdot \max |\, P_{n+1}(x) \,|$.

Folgerung 1. Sei μ_{n+1} ausserhalb des Intervalls genommen, z. B. $\mu_{n+1} > M$, dann hat man für ein beliebiges $Q_n(x)$:

$$-Q_n(\bar{\mu}) + N_{\mu_n} \cdot \max |\, Q_n(x) + x^{n+1} \,| < \mu_{n+1};$$

und nach Multiplikation mit $\alpha > 0$ ergibt sich:

$$N_{\mu_n} \cdot \max |\, \alpha \cdot Q_n(x) + \alpha x^{n+1} \,| < \alpha \cdot \mu_{n+1} + \alpha Q_n(\bar{\mu}).$$

Auf diese Weise entsteht ein symbolisches Polynom, das der verlangten Bedingung nicht genügt. Also passt das gevählte $\mu_{n+1} >$ Mnichtan. (Gleichfalls wenn $\mu_{n+1} < m$).

Folgerum II Wenn man in ähnlicher Weise fortfährt, so erhält man ganz bestimmte Intervalle, in denen die Zahlen μ_{n+1}, $\mu_{n+2}, \ldots$ gewählt werden können und sollen, um die «beste Fortsetzung» der Folge $\mu_0, \mu_1, \ldots, \mu_n$ zu liefern. Wenn $P_n(x) \rightarrow f(x)$, ergibt der Grenzübergang $|\, f(\bar{\mu}) \,| \leqslant N_{\mu_n} \cdot \max |\, f(x) \,|$. Daher ist gemäss den frühereren Resultaten

$$M_{\min} = N_{\mu_n}.$$

Folgerung III. Es sei $\mu_0, \mu_1, \ldots, \mu_{n-1}, \mu_n$ gegeben und es sei festgestellt, dass $N_{\mu_{n-1}} < N_{\mu_n}$. Dann wird die Norm $N_{\mu_n} = M_{\min}$—Norm der besten Fortsetzung—durch ein Polynom genau n-ten (durchans nicht geringeren) Grades erreicht.

Betrachten wir einige Eigenschaften der erreichenden Polynome.

Bemerkung 1. Es ist bekannt (2), dass jede Momentfolge $\mu_0, \mu_1, \ldots, \mu_p, \ldots$ eindeutig als Differenz zweier total monotoner und minimaler Folgen dargestellt werden kann: $\mu_n = \alpha_n - \beta_n$; d. h. es gibt keine absolut monotone Folge (σ), die sich aus (α) und (β) subtrahieren lässt, ohne die Monotonie wenigstens einer von beiden zu stören.

Bezeichnen wir $\pi_{m,n} = \lim\limits_{p} \sum\limits_{k=0}^{p} \binom{p}{k} |\, \mu_{m+k,\, n+p-k} \,|$, so wird $\alpha_n = \frac{1}{2}(\pi_n + \mu_n)$; $\beta_n = \frac{1}{2}(\pi_n - \mu_n)$. Es ist ersichtlich, dass

$$M = \lim_{p} \sum_{0}^{p} \binom{p}{k} |\, \mu_{k,\, p-k} \,| = \pi_0 = \alpha_0 + \beta_0.$$

Aber auch umgekehrt: (α) und (β) bilden das minimale Paar, falls $M = \alpha_0 + \beta_0$ ist. Nämlich, sei (σ) vorhanden, so dass

$$\mu_n = (\alpha_n - \sigma_n) - (\beta_n - \sigma_n) = \alpha'_n - \beta'_n$$

ist, wo (α'); (β') absolut monoton sind, dann ist

$$M = \alpha'_0 + \beta'_0 = \lim \sum \binom{p}{k} |\alpha'_{k,\,p-k} - \beta'_{k,\,p-k}| \leqslant \lim \sum \binom{p}{k} (\alpha'_{k,\,p-k} + \beta'_{k,\,p-k})$$

also $M < \alpha_0 + \beta_0$.

Bemerkung 2. Wenn eine Momentfolge $\mu_0, \mu_1, \ldots \mu_p, \ldots$ mit der Norm M, ein erreichendes Polynom $R_n(x)$ genau n-ten Grades besitzt, d. h. wenn $R_n(\bar{\mu}) = M$ ist, so muss $R_n(x)$ gleichfalls das erreichende Polynom der (α) und (β), die das minimale Paar bilden, sein; daher wird $R_n(\bar{\alpha}) = \alpha_0$; $R_n(\bar{\beta}) = -\beta_0$. (Hier ist $\max |R_n(x)| = 1$ in $(0, 1)$ angenommen.) Allerdings besteht:

$$\mu_n = \alpha_n - \beta_n; \quad M = \alpha_0 + \beta_0 = R_n(\bar{\mu}) = R_n(\bar{\alpha}) - R_n(\bar{\beta});$$

$$\text{aber } |R_n(\bar{\alpha})| \leqslant \alpha_0; \quad |R_n(\bar{\beta})| \leqslant \beta_0.$$

Für die Möglichkeit der Gleichung ist $R_n(\bar{\alpha}) = \alpha_0$ und $R_n(\bar{\beta}) = -\beta_0$ unentbehrlich.

Folgerung. Die notwendige und hinreichende Bedingung für (α), (β), die ein minimales Paar bilden sollen, besteht in der Forderung: das Vorhandensein eines $R_n(x)$ $[\max |R_n(x)| = 1]$ mit den Eigenschaften: $R_n(\bar{\alpha}) = \alpha_0$ und $R_n(\bar{\beta}) = -\beta_0$; denn $R_n(\bar{\mu}) = R_n(\bar{\alpha}) - R_n(\bar{\beta}) = \alpha_0 + \beta_0 \leqslant M$, aber

$$M \leqslant \alpha_0 + \beta_0.$$

Satz 2. *Liegt eine absolut monotone Folge* $\alpha_0, \alpha_1, \ldots, \alpha_n, \ldots, \alpha_p, \ldots$ *vor, so besteht die notvendige und hinreichende Bedingung der Erreichbarkeit von* α_0 *durch ein Polynom genau n-ten Grades darin, dass* α_n *entweder gleich p oder gleich q sein muss, wenn p, q die Grenzen des Intervalls fur* α_n *sind (s. Satz 1).*

1. Nehmen wir an: $p < \alpha_n < q$ und $R_n(x) = \Sigma r_i x^i$ sei das erreichende Polynom, also $R_n(\bar{\alpha}) = \alpha_0$. Wir ersetzen α_n erstens durch $p = \alpha_n - b_1$ und zweitens durch $q = \alpha_n + b_2$, wo $b_1 > 0$; $b_2 > 0$. Wir bezeichnen $\alpha_0, \alpha_1, \ldots, \alpha_{n-1}, p$ mit (α') und $\alpha_0, \alpha_1, \ldots, \alpha_{n-1}, q$ mit (α''); dann bekommen wir:

$$|R_n(\bar{\alpha}')| = |\alpha_0 - r_n b_1| \leqslant \alpha_0,$$

d. h. $r_n \geqslant 0$,

$$|R_n(\bar{\alpha}'')| = |\alpha_0 + r_n b_2| \leqslant \alpha_0,$$

d. h. $r_n \leqslant 0$ folglich $r_n = 0$.

Also ist $\alpha_n = p$ bzw. $\alpha_n = q$, so hat man für das erreichende Polynom: $r_n < 0$ bzw. $r_n > 0$.

2. Es sei in der gegebenen absolut monotonen Momentfolge $\alpha_0, \alpha_1 \ldots, \alpha_n, \ldots, \alpha_p, \ldots, \alpha_n = p$. Nehmen wir an, es fehle unter $\{P_n(x)\}$ mit $\max |P_n(x)| = 1$ und genau n-ten Grades ein erreichendes Polynom, also für alle $P_n(x)$ ist folgendes gültig: $|P_n(\bar{\alpha})| < \alpha < \alpha_0$. Wir ersetzen α_n in der endlichen Folge $\alpha_0, \alpha_1, \ldots, \alpha_n$ durch $p - \varepsilon$ mit $\varepsilon < 0$ und bezeichnen sie mit (α'). Nach Satz 1 ist (α') nicht monoton, und dabei angefan-

gen von α_n; dann aber darf man die Existenz eines $Q_n(x)$ behaupten, für den $Q_n(\alpha') > \alpha_0$ ist; so hat man für genügend kleines ε:

$$|Q_n(\alpha')| = |Q_n(\alpha) - q_n\varepsilon| < \alpha + |q_n| \cdot \varepsilon < \alpha_0,$$

was aber der Voraussetzung widerspricht *.

Auf ähnliche Weise wird der Beweis für $\alpha_n = q$ durchgeführt.

Ist also $\alpha_0, \alpha_1, \ldots, \alpha_n, \ldots$ asbolut monoton, so gibt es erreichende Polynome aller solcher Grade k (und zwar nur solcher), wo α_k an der Grenze seines Intervalls liegt (oder eindeutig bestimmt ist).

Verallgemeinerung des Satzes 2. Es sei eine beliebige endliche Folge: $\mu_0, \mu_1, \ldots, \mu_n$ gegeben. Wir setzen sie in der besten Weise fort (s. I. Teil); dann ist $M_{\min} = N_{\mu_n}$. Nach Bemerkung 1 kann man $\mu_n = \alpha_n - \beta_n$ setzen, wo (α) und (β) das minimale Paar bilden, und $M_{\min} = \alpha_0 + \beta_0$ ist. Sei ausserdem $N_{\mu_n} > N_{\mu_{n-1}}$. Dann existiert (s. I. T.) $R_n(x)$ genau n-ten Grades, so dass $R_n(\bar{\mu}) = M_{\min}$ und folglich

$$R_n(\alpha) = \alpha_0;\ R_n(\bar{\beta}) = -\beta_0.$$

Nach Satz 2 müssen α_n und β_n beide an den entsprechenden Grenzen liegen. Wenn es erlaubt wird α_n für gegebene $\alpha_0, \alpha_1, \ldots, \alpha_{n-1}$, bzw. für β_n $\beta_0, \beta_1, \ldots, \beta_{n-1}$ im Intervalle $m_1 \leqslant \alpha_n \leqslant m_2$ bzw. $n_1 \leqslant \beta_n \leqslant n_2$, zu wählen, so ist entweder $\alpha_n = m_1$ und dann ist $r_n < 0$; also wegen $R_n(\beta) = -\beta_0$, muss $\beta_n = n_2$ sein; oder ist $\alpha_n = m_2$ dann muss $\beta_n = n_1$ sein; da aber das möglichst grosse Intervall für μ_n genau mit $m_1 - n_2 \leqslant \alpha_n - \beta_n \leqslant m_2 - n_1$ übereinstimmt, so lautet das Resultat: Wenn μ_n die beste Fortsetzung geben sollte, so hat man für μ_n eine der Grenzzahlen zu nehmen.

Beispiel 1. $1, \frac{1}{2}, \frac{1}{3}, \ldots, \frac{1}{n+1}, \ldots = (\alpha)$ ist absolut monoton. Ihre Norm 1 wird von keinem Polynom erreicht, wenn sein Grad $n \geqslant 1$ ist.

Nämlich, sei $\max |R_n(x)| = 1$. Dann hat man

$$|R_n(\bar{\alpha})| = \left|\int_0^1 R_n(x)dx\right| < 1.$$

Daraus folgt: $\alpha_1, \alpha_2, \alpha_3$ u. s. w. gehören dem Inneren der entsprechenden Intervalle.

Beispiel 2. $1, \frac{1}{2}, \frac{1}{4}, \ldots, \frac{1}{2^k}, \ldots$ ist absolut monoton. Ihre Norm 1 wird durch wohlbestimmte Polynome aller gleichen Grade $2n \geqslant 2$ erreicht, nämlich durch $R_{2n}(x) = (-1)^n \cdot T_{4n}(\sqrt{x})$, wo T das Polynom von Tschebyscheff bedeutet; dabei liegt $a_k = \frac{1}{2^{4k+2}}$ auf der unteren Grenze, und $a_k = \frac{1}{2^{4k}}$ auf der oberen.

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ZITIERTE LITERATUR

[1] E. Voronovsky, C. R. Acad. Sci URSS, I, № 3 (1936); [2] Hausdorff, Math. Ztschr. (1921).

* $|q_n'|$ ist begrenzt, denn $q_n = P_n(\nu)$, wo $(\nu) = 0{,}0, \ldots, 0{,}1_n$ zu wählen ist.

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PHYSIQUE

DIFFRACTION DE LA LUMIÈRE PAR DES ULTRA-SONS

Par S. M. RYTOV

(Présenté par L. J. Mandelstam, de l'Académie, le 25. VI. 1936)

1. Dans la note précédente (1) j'ai indiqué une méthode permettant de trouver une solution approchée du problème de la diffraction de la lumière sur les ultra-sons, solution qui dans le cas limite $\Lambda \to \infty$ (Λ étant la longueur de l'onde ultra-sonore) conduit aux résultats de la théorie de Raman-Nath (2). L'analyse plus détaillée que je donne ici établit dans quelles conditions on peut s'en tenir aux quantités du 1-er ordre en α (α étant le «taux de modulation» de l'indice de réfraction), notamment pour le cas $\Lambda = \infty$, c'est-à-dire dans quelles conditions est valable la théorie de Raman-Nath (R.-N.). J'ai pus également établir le rapport, qui existe entre mon résultat et ceux que donnent certaines autres méthodes de calcul approché.

J'ai trouvé que là où il est légitime de se limiter aux grandeurs du premier ordre en α, ma solution ne corrige que très légèrement les résultats de R.-N. La raison en est que, Λ racourcissant, les valeurs de α pour lesquelles on peut négliger α^2 etc. diminuent rapidement. Pour la même raison la théorie de R.-N. n'est applicable dans les conditions pratiquement les plus intéressantes que s'il n'existe qu'un nombre très restrein de spectre de diffraction.

2. Le procédé de calcul dont je me suis servi consistait à faire dans l'équation:

$$\frac{\partial^2 E_0}{\partial \zeta^2} + \beta \frac{\partial^2 E_0}{\partial \xi^2} + (1 + \alpha \cos \xi)^2 E_0 = 0, \qquad (1)$$

où

$$\zeta = \frac{2\pi\mu_0}{\lambda_0} z, \quad \xi = \frac{2\pi}{\Lambda} x, \quad \beta = \frac{\lambda_0^2}{\mu_0^2 \Lambda^2},$$

la substitution

$$E_0 = e^{\psi(\zeta, \xi)} \qquad (2)$$

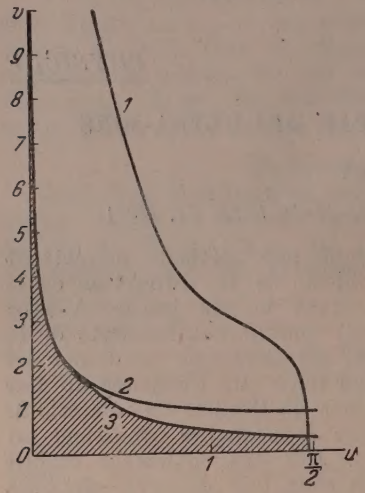
et à chercher ψ sous forme de série de la forme:

$$\psi = -i\zeta + \alpha\psi_1 + \alpha^2\psi_2 + \cdots.$$

Négligeant α^2 devant 1 on a pour ψ l'équation:

$$\frac{\partial^2 \psi}{\partial \zeta^2} + \beta \frac{\partial^2 \psi}{\partial \xi^2} + \left(\frac{\partial \psi}{\partial \zeta}\right)^2 + \beta \left(\frac{\partial \psi}{\partial \xi}\right)^2 + 1 + 2\alpha \cos \xi = 0. \qquad (3)$$

On peut montrer que supprimer $\frac{\partial^2\psi}{\partial\zeta^2}$, c'est-à-dire passer partiellement à l'optique géométrique (à l'équation de l'eiconal) équivaut à négliger dans tous des ψ_n des termes qui dans les conditions pratiques ($\zeta \sim 10^5$) sont de l'ordre de 10^{-5} par rapport aux termes principaux et qui, de plus, oscillent rapidement en fonction de z (leur période est tout au plus de l'ordre de grandeur $\frac{\lambda_\eta}{2\mu_0}$). Ensuite, étant donné que $\beta \sim 10^{-5}$, il est possible de ne maintenir dans les seconds membres des équations pour les ψ_n que les dérivées par rapport à ξ, ce qui équivaut à ne conserver dans les ψ_n que les termes dont les dénominateurs contiennent la plus grande puissance de β. On obtient le système:



$$\left.\begin{aligned}
&\frac{\partial\psi_1}{\partial u} + i\frac{\partial^2\psi_1}{\partial\xi^2} = -\frac{2}{\rho}\cos\xi,\\
&\frac{\partial\psi_2}{\partial u} + i\frac{\partial^2\psi_2}{\partial\xi^2} = -\left(\frac{\partial\psi_1}{\partial\xi}\right)^2,\\
&\frac{\partial\psi_3}{\partial u} + i\frac{\partial^2\psi_3}{\partial\xi^2} = -2\frac{\partial\psi_1}{\partial\xi}\frac{\partial\psi_2}{\partial\xi},\\
&\cdots\cdots\cdots\cdots
\end{aligned}\right\}$$

où

$$u = \frac{\beta\zeta}{2} = \frac{\pi\lambda_0 z}{\mu_0 A^2}.$$

Les conditions aux limites sont

$$u = 0, \quad \psi_n = 0\,(n = 1, 2, 3\ldots),$$

L'intégration de ces équations donne

$$\psi = -i\zeta + \rho a(u)\cos\xi + \rho^2[b(u) + c(u)\cos 2\xi] + \\ + \rho^3[d(u)\cos\xi + e(u)\cos 3\xi] + \ldots, \qquad (4)$$

où

$$\rho = \alpha\zeta = \frac{2\pi\mu_0 z}{\lambda_0}\alpha$$

(ρ est l'argument des fonctions de Bessel qui figurent dans la théorie de R.-N.) et

$$\left.\begin{aligned}
&a(u) = \frac{1}{u}(1 - e^{iu}),\\
&b(u) = \frac{1}{4u^2}(-e^{2iu} + 4e^{iu} - 2iu - 3),\\
&\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned}\right\}$$

Lorsque $u \to 0$, ψ_n tend vers zéro comme u^{n-1}; donc $a(0)$ seulement est différent de zéro et égal à $-i$. Par conséquent,

$$\psi_{u=0} = -i(\zeta + \rho\cos\xi) = -i(1 + \alpha\cos\xi)\zeta, \qquad (5)$$

ce qui correspond à l'expression initial de la théorie de R.-N.

$$E_0 = e^{-i(1+\alpha\cos\xi)\zeta}.$$

Développant dans (4) $a, b, c, \ldots$ suivant les puissances de u et réunissant les termes contenant la même puissance de u on a:

$$\psi = -i(\zeta + \rho\cos\xi) + u\rho\left(\frac{i\rho\sin^2\xi}{3} + \frac{\cos\xi}{2}\right) +$$

$$+ u^2\rho\left[\frac{4i\rho^2\sin^2\xi\cos\xi}{15} + \frac{\rho(5-7\sin^2\xi)}{12} + \frac{i\cos\xi}{6}\right] + \cdots \qquad (6)$$

Ce résultat s'obtient directement si l'on cherche la solution de (3) (en faisant les simplifications permises, analogues à celles indiquées plus haut) sous forme de série suivant les puissances de β. Enfin dans le cas où, considérant u comme très petite, on ne maintient dans les coefficients des ρ_n que la plus petite puissance de u, on a:

$$\psi = -i(\zeta + \rho\cos\xi) + \frac{i\rho^2 u}{3}\sin^2\xi + \frac{4\,i\rho^3u^2}{15}\sin^2\xi\cos\xi + \cdots. \qquad (7)$$

On voit facilement que (7) est le résultat que l'on obtiendrait en négligeant dans (3) non seulement $\frac{\partial^2\psi}{\partial\zeta^2}$, mais aussi $\frac{\partial^2\psi}{\partial\xi^2}$, c'est-à-dire en passant complètement à l'optique géométrique [hypothèse de la théorie de Lucas et Biquard (3)]. Naturellement, dans le dernier cas également (5) est une valeur limite—fait dont l'intérprétation géométrique est suffisamment connue. On peut obtenir (7) en cherchant la solution de l'équation de l'eiconal indifféremment sous forme de série en α ou en β.

3. Les amplitudes lumineuses dans les faisceaux diffractés peuvent être exprimées simplement à l'aide de fonction de Bessel dans le cas seulement, où l'on se limite dans (4) à la première puissance de ρ. Comme il a déjà été montré (1), l'amplitude dans le n-ème spectre est proportionnelle à

$$J_n\left(\rho\,\frac{\sin\frac{u}{2}}{\frac{u}{2}}\,e^{i\frac{u}{2}}\right), \qquad (8)$$

ce qui donne pour $u = 0$ l'expression de R.-N.

$$J_n(\rho). \qquad (9)$$

Etant donné qu'en réalité $u \neq 0$, la validité de (9) pour toutes les valeurs de ρ n'est qu'apparente. La question qui se pose est de savoir quand l'expression (8) est-elle valable et quel est le degré d'approximation donné par (9), ou bien de savoir dans quelles conditions on peut négliger dans (6) tous les termes dépendant de u. Comparant les arguments de (8) et de (9) j'ai conclu précedemment que la théorie de R.-N. est suffisamment exacte pour $u < \frac{\pi}{6}$. Une analyse plus approfondie perment de préciser ce critérium.

Il est évident que (9) ne possède une interprétation physique que jusqu'à $u \cong \frac{\pi}{2}$, car à partir de cette valeur et à peu près jusqu'à $u = \frac{3\pi}{2}$ nous sommes dans un domaine où pour tous les $\rho \neq 0$ $|J_0| > 1$, c'est-à-dire l'intensité du faisceau d'ordre 0 dépasse celle de l'onde primitive. On ne peut donc utiliser lorsque $u \geqslant \frac{\pi}{2}$ (pratiquement u peut atteindre la valeur 20) simplement les fonctions de Bessel; en

d'autres termes il est inadmissible de se borner dans ψ aux grandeurs du premier ordre en α.

Quant au domaine $u < \frac{\pi}{2}$, la condition $|J_0| \leqslant 1$ y limite les valeurs admissible de φ de la façon que montre la courbe *1* de la figure. Mais cette condition n'est pas la plus restrictive. En effet, pour que l'on puisse se limiter dans (4) aux grandeurs du premier ordre en φ et dans (6) à l'approximation zéro, il faut que les séries convergent assez rapidement. Le calcul de ψ terme à terme ne permet pas de résoudre la question de convergence d'une façon complète, mais conduit néanmoins à certaines restrictions dont l'interprétation physique est assez claire.

Nous pouvons demander, par exemple, que dans (4) le terme en φ^2 ait un module $\ll 1$ même pour les valeurs les plus défavorables de ξ (égales à ξ_m):

$$\varphi^2 | b(u) + c(u) \cos 2\xi_m | \ll 1.$$

Le calcul montre que pour $u < \frac{\pi}{2}$ cette condition est restrictive surtout pour $\xi_m = \left(n + \frac{1}{2}\right)\pi$, étant de la forme:

$$\varphi^2 | b(u) - c(u) | \ll 1. \qquad (10)$$

Remplaçant $\ll 1$ par $= \frac{1}{4}$, nous obtenons la courbe *2* de la figure.

On peut traiter de la même façon le terme du 1-er ordre en u de (6), ce qui donne les conditions:

$$\left.\begin{array}{l} \frac{\varphi^2 u}{3} \ll 1, \text{ pour } \varphi > \frac{3}{2} \quad \left[\xi_m = \left(n + \frac{1}{2}\right)\pi\right]. \\ \frac{\varphi u}{2} \ll 1, \text{ pour } \varphi < \frac{3}{2} \quad (\xi_m = n\pi). \end{array}\right\} \qquad (11)$$

Remplaçant là aussi $\ll 1$ par $= \frac{1}{4}$, nous obtenons la courbe *3*. Les conditions (11) ne sont que légèrement plus restrictives que (10), mais beaucoup plus restrictives par rapport à φ que la condition $|J_0| \leqslant 1$) (courbe 1). Remarquons que la considération des approximations suivantes dans (4) et (6) n'affaiblit pas les conditions (10) et (11).

Admettant maintenant que sur la figure la région ombrée limitée par les courbes *3* et *1* est celle où la théorie de R.-N. est applicable [et avec elle la formule (8)], on voit facilement que (8) et (9) y sont presque identiques. Quant aux frontières de cette région, on peut les exprimer sous une forme plus commode. On peut, d'une part, tirer de (9) le «seuil» d'apparition du spectre d'ordre n, c'est-à-dire trouver la valeur de $\varphi = \frac{2\pi\mu_0 z\alpha}{\lambda_0}$ pour laquelle son intensité atteint, par exemple, 1% de celle de la lumière incidente ($J_n^2(\varphi) = 0.01$). D'autre part, on peut indiquer dans la région ombrée pour tous les φ trouvés de cette façon la valeur maximum de $u = \frac{\pi\lambda_0 z}{\mu_0 \Lambda^2}$ pour laquelle la formule (9) vaut encore. Ces valeurs optimales de u, z et λ_0 étant données, déterminent les plus petites valeurs admissibles de Λ. Pour $z = 2$ cm, $\mu_0 = 1.5$ et $\lambda_0 = 4\,000$ Å et $8\,000$ Å on obtient le tableau suivant:

Le spectre d'ordre $n=$ apparaît	1	2	3	4	5	8	16
lorsque $v=$	0.21	0.95	1.85	2.75	3.75	6.70	14.80
$u<$	$\frac{\pi}{2}$	0.53	0.22	0.10	0.053	0.017	0.0035
$\lambda_0 = 4\,000$ Å, Λ (mm) $>$	0.03	0.18	0.28	0.41	0.56	1.00	2.21
$\lambda_0 = 8\,000$ Å, Λ (mm) $>$	0.04	0.25	0.39	0.58	0.79	1.42	3.13

Ainsi, lorsque pour $\Lambda = 0.2$ mm il existe un spectre de 3-ème ordre la réparation de l'énergie ne peut plus être calculée à l'aide de la théorie de R.-N., comme le montrent d'ailleurs les résultats expérimentaux de Bär (4), qui trouva que pour $z = 2$cm, $\lambda_0 = 5\,461$ Å la téorie de R.-N. est en accord avec les mesures pour la fréquence $1\,500 \cdot 10^3$ sec.$^{-1}$ ($\Lambda = 0.88$ mm dans le xylol) et en désaccord pour la fréquence $7\,500 \cdot 10^3$ sec.$^{-1}$. Dans le premier cas, à en juger par les photographies, $n = 5$, dans le second, $n = 4$.

4. J'indique, pour terminer ma note, dans quel rapport est la solution (2) avec celle de Brillouin (5), qui s'écrit, en employant mes notations:

$$E_0 = e^{-i\left(\zeta + \frac{v^2}{2u} + \dots\right)} \left\{ 1 + \frac{v}{u} \left[1 - e^{iu\left(1 + \frac{11v^2}{12u^2} + \dots\right)} \right] \cos\xi + \right.$$
$$+ \frac{v^2}{4u^2} \left(2 \left[e^{iu\left(1 + \frac{11v^2}{12u^2} + \dots\right)} - 1 \right] + \right.$$
$$\left. \left. + \left[\frac{1}{2} - \frac{2}{3} e^{iu\left(1 + \frac{11v^2}{12u^2} + \dots\right)} + \frac{1}{6} e^{4iu\left(1 + \frac{2v^2}{15u^2} + \dots\right)} \right] \cos 2\xi \right) + \dots \right\} \qquad (12)$$

La solution de Brillouin (développement en série de fonctions de Mathieu) est, comme on le sait, absolument rigoureuse en principe, mais pour le calcul on doit développer les fonctions de Mathieu elles-mêmes, les valeurs propres et les coefficients de la série en séries de puissances de $\frac{v}{u}$ $\left(= \frac{h^2}{2}\right.$ dans les notations de Brillouin$\left.\right)$.

Introduisant (4) dans (2) et développant E_0 suivant les puissances de v nous avons

$$E_0 = e^{-i\zeta} \left\{ 1 + \frac{v}{u} (1 - e^{iu}) \cos\xi + \frac{v^2}{4u^2} \left(2 [e^{iu} - 1 - iu] + \right.\right.$$
$$\left.\left. + \left[\frac{1}{2} - \frac{2}{3} e^{iu} + \frac{1}{6} e^{4iu} \right] \cos 2\xi \right) + \dots \right\}. \qquad (13)$$

Le rapport $\frac{v}{u}$ étant indépendant de l'épaisseur z de colonne ultra-sonore (u et v étant proportionnels à z), on peut énoncer la différence entre (12) et (13) de la façon suivante. Dans (12) les coefficients de cos $n\xi$ sont des sommes de termes périodiques en z, dont les périodes dépendent de $\frac{v}{u}$, c'est-à-dire non seulement de Λ et λ_0, mais aussi de l'intensité de

l'onde ultra-sonore (a). Dans (13) les coefficients contiennent des termes périodiques en z de périodes indépendantes de α et des termes non périodiques. On voit facilement d'où vient la différence: la formule (13) s'obtient si l'on développe les exposants de (12) suivant les puissances de $\frac{v}{u}$.

On obtiendra directement la formule (13) en résolvant l'équation (1), préalablement simplifiée comme nous l'avons fait pour (3), à l'aide d'une série suivant les puissances de α.

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HYDROTECHNIK

EINFLUSS DER BODENKAPILLARITÄT AUF DIE SICKERSTRÖMUNG MIT FREIER OBERFLACHE

Von V. V. WEDERNIKOV

(Vorgelegt von N. N. Pavlovskij, Mitglied der Akademie d. 7 V 1936)

Die Oberflächenspannung ist in ihrer Einwirkunng auf den Wassermeniskus in den Kapillarschlitzen des Bodens gleichbedeutend mit der Wirkung eines Vakuums von der Höhe h_v. Da der Boden die Eigenschaften eines solchen Vakuums aufweist, so ergibt sich, dass der Wasserdruck auf der freien Oberfläche des durchsickernden Wassers nicht dem Atmosphärendruck gleich ist, sondern einen Unterdruck von der Grösse des Bodenvakuums h_v darstellt. An der freien Oberfläche ist daher das Geschwindigkeitspotential:

$$\varphi = k_\varphi (y + h_v). \qquad (1)$$

Diese Beschaffenheit des Bodens bewirkt, dass Strömungsbild und Druckverteilung im Sickerstrom wesentlich verändert werden. Um ein Schema

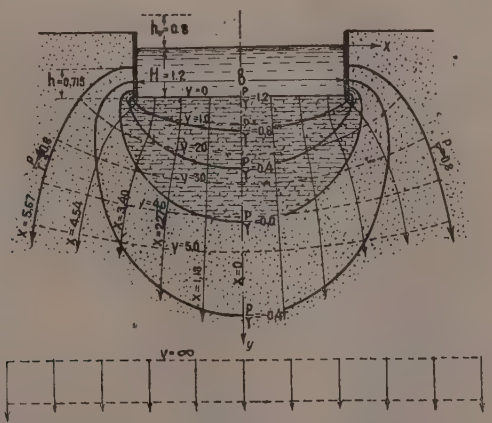

Abb 1.

für den Sickerungsvorgang bei dieser Bodenbeschaffenheit aufzustellen, betrachten wir den Fall einer Sickerung ohne Stau aus einem durch Spundwände gebildeten Kanal (Abb. 1), die bis zur Tiefe d unterhalb

der Kanalsohle eingerammt sind. Die Lösung liesse sich im gegebenen Fall durch folgende Gleichungen ausdrücken [s. auch (1)]:

$$\theta_1 + i\theta_2 = x - X + i \cdot (y - Y - H) = D \int_0^{\zeta} \frac{d\zeta}{\sqrt{1-\zeta^2}\sqrt{k^2-\zeta^2}}, \qquad (2)$$

$$X^2 + iY = i\frac{\varphi + i\psi}{k_\varphi} = q \int_0^{\zeta} \frac{d\zeta}{\sqrt{k^2-\zeta^2}} = q \arcsin \frac{\zeta}{k}, \qquad (3)$$

$$\text{wo } q = \frac{Q}{\pi k_\varphi} \text{ und } D = -\frac{H_v}{K_1}.$$

Die Formel, die zur Bestimmung der Sickerwassermenge pro Längeneinheit des Kanals benutzt wird, lautet dann folgendermassen:

$$Q = k_\varphi \cdot \left(b + 2H_v \frac{K}{K_1}\right). \qquad (4)$$

In Abb. 1 ist der Verlauf der Linien gleichen Druckes, sowie auch das Strömungsbild für den Fall $\alpha = \arcsin k = 70°$, $H = 1.2$ m, $d = 0$, $h_v = 0.8$ m, $H_v = 1.2 + 0.8 = 2.0$ m und $b = 5.156$ m dargestellt. Verfassers tellt das Vorliegen zweier Zonen fest: a) einer Zone des «Grundwassers, wo $\frac{P}{\gamma} \geqslant \frac{P\alpha}{\gamma}\left(^2\right)$ (schraffiert in Abb. 1 und b) einer Vakuumszone oder Kapillarzone. Ausserdem gibt er auch

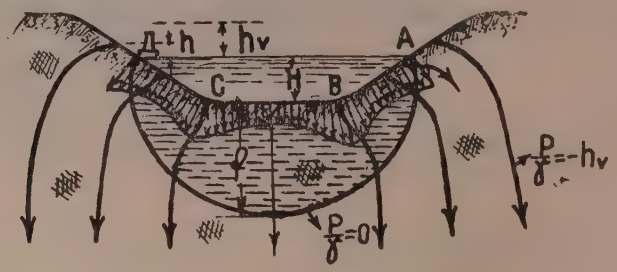

Abb 2.

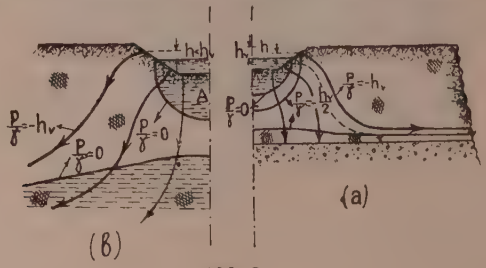

Abb 3.

ein Übergangsbild von der einen Zone in die andere an. Legt man das Schurfloch in einer Zone an, in welcher der Wasserdruck geringer ist als der Luftdruck, so wird offenbar das Sickerwasser nicht ausfliessen, obwohl sich das Wasser auch hier in Bewegung befindet. Das Sickerwasser würde bestrebt sein, das Schurfloch zu umgehen, wenn der Druck in der Nähe des Schurfloches infolge

Veränderungen, die im Sickerstrom durch Einbringen des Schurflöches erzeugt wurden, nicht höher als der Luftdruck wäre. Für den in Abb. 1 dargestellen Fall ist der Einfluss des Bodenvakuums auf die Sickerwassermenge gleichbedeutend mit einer Zunahme der Kanalwassertiefe um die Höhe h_v. In Abb. 2 ist die Kanalversickerung, sowie auch die Druckverteilung im Sickerstrom und die Sickergeschwindigkeitsverteilung längs des benetzten Kanalumfanges schematisch dargestellt. Die Höhe, bis zu welcher das Wasser an der Böschung über den Wasserspiegel im Kanal emporsteigt, ist weit geringer als die Höhe des Kapillaren Anstiegs, denn das längs der Böschung

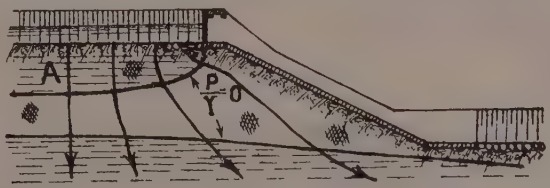

Abb 4.

sichernde Wasser befindet sich nicht im Ruhezustand. In der Praxis ist ein Zerfliessen des Sickerstroms über die Grenzen der unteren, bei weitem durchlässigeren Schicht hinaus erforderlich (Abb. 3, *a*), was z. B. auch über der Drainage eines Erddammes der Fall ist.

Abb. 3, *б* veranschaulicht die Sickerung aus Kanälen bei verhältnismässig-niedrigem Grundwasserstand, sowie auch die Druckverteilung im Sickerstrom. Je nach den Abmessungen des Kanals und der Tiefe des Grundwasserspiegels wird zwischen der in der Nähe der Kanalsohle befindlichen Zone *A* und dem Grundwasserspiegel eine Unterdruckzone (Vakuumzone) liegen, oder aber die Zone *A* fliesst mit dem Grundwasser zusammen. Abb. 4 stellt, entspre-

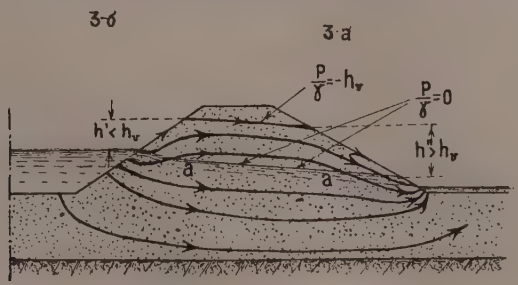

Abb 5.

chend der Abb. 3, *b*, die Druckverteilung im Sickerstrom unterhalb einer Wasseranlage im Zuge von Kanälen dar, unter Berücksichtigung der kapillaren Aufstiegswirkung des Grundes. Je nach dem Grade des Zusammenfliessens der Zone *A* mit dem Grundwasser ist auch mit der Wahrscheinlichkeit einer Druckwirkung auf die Fundamentsohle der Anlage zu rechnen. Abb. 5 stellt das Bild des Sickerungsvorganges bei Erddämmen unter Berücksichtigung des «Grundvakuums» dar.

Verfasser [vgl ([3])] stellt fest, dass zwischen der Bewegung des Wassers in der Grundwasserzone und der in der Kapillarzone ein Zusammenhang besteht und dass sie ein unzertrennliches Ganzes bilden. Des ferneren gibt er auch

Bilder des Übergangs von der einen Zone in die andere, sowie auch die Bedingungen, unter denen dieser Übergang stattfindet, wieder. Die «Sickerlinie» *a-a*, d. h. die Luftdruckslinie oder der «Grundwasserspiegel» ist weder eine freie Oberfläche noch überhaupt eine Stromlinie und daher auch keine Senkrechte zur benetzten Böschung usw. Der rechte Teil der Abb. 5 entspricht dem Bild des Wasserzustroms zu Entwässerungsgraben, Brunnen usw.

Das die Bodenporen eine Siphonartige Hebewirkung ausüben können wurde durch die von Žukovsky (4), Laughlin (5) und Rehbock (6) angestellten Versuche nachgewiesen.

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CHEMISTRY

ON THE EVOLUTION OF SULPHUR OXIDES FROM CALCIUM SULPHATE BY MEANS OF CHLORINE, IN THE PRESENCE OF CATALYZERS, FOR SIMULTANEOUS PRODUCTION OF HYDROCHLORIC AND SULPHURIC ACID

By P. P. BUDNIKOV (BUDNIKOFF) and E. I. KREČ (KRETCH)

(Communicated by N. S. Kurnakov, Member of the Academy, 16. IV. 1936)

The existing methods of treatment of gypsum [1] are practically limited to its complex utilization for obtaining sulphur or its oxides and Portland cement.

The purpose of our investigations was, in the first place, to establish the conditions of the maximum evolution of sulphur oxides from calcium sulphate by means of chlorine, our intention being to attain this by means of catalyzers (K) or additions (*e. g.* sand), according to the general schemes of the principal processes shown below:

$$CaSO_4 + Cl_2 + (K) \rightarrow CaCl_2 + SO_2 + O_2 + (K), \quad (1)$$

$$CaSO_4 + SiO_2 + Cl_2 \rightarrow CaSiO_3 + CaCl_2 + SO_2 + O_2, \quad (2)$$

and, in the second place, to utilize the by-products ($CaSiO_3 + CaCl_2$), which it was proposed to use to obtain a mixture of $CaSiO_3$, CaO and SiO_2, utilizable in the ceramic, glass and other industries, by treating the residue remaining after chlorination by vapour, according to the third scheme:

$$CaCl_2 + SiO_2 + H_2O \text{ (vapor)} \rightarrow CaSiO_3 + 2HCl, \quad (3)$$

and, in the third place,—to obtain HCl and H_2SO_4 from the gases formed according to schemes (4), (5), (6):

$$SO_2 + H_2O \rightarrow H_2SO_3, \quad (4)$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl, \quad (5)$$

$$H_2SO_3 + HOCl \rightarrow H_2SO_4 + HCl. \quad (6)$$

The processes expressed by schemes (1), (2) and (3) proved to be the least studied. Therefore the principal attention was paid to processes (1), and (2), the 3rd having been studied by A. Moissan [2], and our preliminary experiments having given encouraging results. Many investigators [3] have studied and are still studying the processes expressed by schemes (4), (5) and (6). This problem has been studied for nearly a hundred years and it has been found that the utilization of SO_2 and Cl_2 according to schemes (4), (5) and

(6) attains 100% and that the process of obtaining HCl and H_2SO_4 is not a complicated operation and can be successfully used in industry.

EXPERIMENTAL PART

Reagents. A chemically pure Kahlbaum $CaSO_4$ was used in all investigations excepting the work with the pure preparation (Table 1); it was heated in a double platinum crucible at 600—650° to constant weight, with 58.8% content of SO_3 according to our analytical data.

A standard electrolytical chlorine containing about 99.5% of chlorine was used in all experiments.

The SiO_2 taken in nearly all experiments was in the form of Tchasov-Yar sand burnt at 600—650° during three hours and subsequently ground (residue on 10 000 mesh/cm² screen—16.5%). The mean composition of dried sand in per cent was as follows:

Ignition loss	0.12%
SiO_2	98.50%
Al_2O_3	0.59%
Fe_2O_3	0.54%
CaO	0.13%
MnO	traces
Total	99.98

Cristobalitized Tchasov-Yar sand was obtained by heating a sample of 1 550° during one hour, with subsequent fine grinding in an agate mortar. Fineness of grind: residue on a 10 000 mesh/cm² screen—8.6%.

The SiO_2 remaining after the analysis of silicates was dried to constant weight at 130—150°, ground in an agate mortar and screened with 10 000 mesh/cm² screen leaving no residue.

Silica-gel was obtained by precipitation with hydrochloric acid from a Na_2SiO_3 solution washed until no reaction with chlorin ions took place, dried at 110—115° to constant weight, reduced to powder and screened (residue on a 10 000 mesh/cm² screen—6.2%).

Rock crystal was taken from a big transparent crystal, reduced to powder first in an Abich and than in an agate mortar, washed free of the iron of the mortar with a warm solution of HCl, dried to constant weight at 150° and screened with a 10 000 mesh/cm² screen; residue on screen ~ 12%.

Fused quartz was obtained from opaque quartz tubes and prepared in the same way as rock crystal. Residue on a 10 000 mesh/cm² screen—9%.

Anal. pure Na_2SO_4 was dehydrated at 550—600°. After dehydration it contained, according to analytical data, 56.62% SO_3.

$CuSO_4 \cdot 5H_2O$, anal. pure, and $MgSO_4$ were dehydrated at 225° (4).

$NiSO_4$ and anal. pure $MnCl_2$ were dehydrated at 290°(4).

Anal. pure KCl, MnO_2 and Fe_2O_3 were dried at 170—190°.

The mixtures prepared were analyzed for SO_3.

Apparatus and methodics of investigations. The chlorination of the samples was carried out in the apparatus shown in the appended scheme and consisting of: a metallic tank filled with chlorine (*1*), a washer (*2*) with H_2SO_4, sp. gr. 1.84, a rheometer (*3*) scaled to the pressure yielded by a series of bottles (*4* and *5*) filled with H_2SO_4, sp. gr. 1.84, for the drying of chlorine, and with glass wool (*6*) to retain such drops of H_2SO_4 as might possibly form owing to the rapid flow of chlorine. The chlorine so dried was, first, admitted into a three-way glass pipe (*8*), then into an unglazed porcelain pipe (*9*) introduced into resistance furnace (*10*) with a platinum winding and a rheostat (*11*); then it passed under an

unglazed porcelain $60 \times 11 \times 14$ mm boat (*12*) and entered the drougt together with the flue (exhaust) gases. Temperature measurements were made with a Le Chatelier thermocouple (*7*) provided with a millivoltmeter. Pyrometer readings were checked against the fusing temperatures of salts and with a Siemens precision pyrometer.

In every case, 1.0000 g of the prepared mixture of $CaSO_4$ with an addition was put into the boat. The boat was introduced into the furnace heated to the temperature of the experiment either at once or gradually, if NaCl and SiO_2 formed a part of the mixture, because when cracking at high temperatures

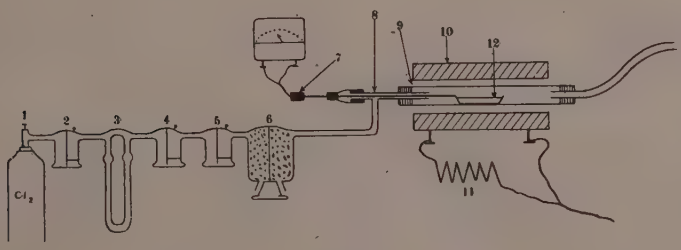

Fig. 1.

they can toss out a part of the contents of the boat. After this, chlorine was introduced at a mean velocity of 0.1 l/min; the operation lasting an hour in every case.

After chlorination, the boat was pushed out of the furnace with a porcelain tube (pipe), was cooled, and in order to determine the percentage of SO_3 was placed in a glass with boiling water or with a solution of HCl, where the residue left after chlorination was separated from the boat. The filtrate obtained in either way from the contents of the boat was used for the determination of the percentage of SO_3 present in form of $BaSO_4$.

The calculation of the yields made by the writers in respect to SO_3, is a conditional one, owing to the dissociation of SO_3, which begins at temperatures above 450° and ends completely at 1000°. If the chlorination of $CaSO_4$ takes place in the presence of coal, SO_3 and SO_2 are not necessarily formed.

Chlorination of $CaSO_4$, either pure or in the presence of catalyzers and additions.

In the first stage of our investigations pure $CaSO_4$* was subjected to the action of chlorine; it was observed as this can be seen from table 1, that a rise of tempetarure increases the velocity of the reaction (according to scheme), the yield of SO_3 being nearly 100% at 1 100—1 150°.

Later on, in order to lower the temperature of the reaction and to increase the velocity of the extraction of SO_3 the following substances were added to the $CaSO_4$: 44.1% SiO_2 in the form of Tchasov-Yar sand, 11.4% Na_2SO_4, 10% NaCl or 44.1% SiO_2 and 6.8% Na_2SO_4 calculated on the weight of the mixture of the first two constituents and the chlorination was carried out as described above.

* This part of the work has been fulfilled by E. Kretch and J. Kolodkina at the White Russian Academy of Sciences in 1934—1935.

The data of these experiments shown in table 1 demonstrate that the addition of SiO_2, Na_2SO_4, NaCl to $CaSO_4$ or the addition of Na_2SO_4 to the mixture of $CaSO_4$ and SiO_2 increase the yield of SO_3,

Table 1

№	Substance investigated	SO_3 content in the initial substance	SO_3 yield in % to residue in boat at temperature °C				
			700—750	800—850	900—950	1 000—1 050	1 100—1 150
1	$CaSO_4$	57.0	—	1.9	4.9	23.5	97.9
2	$CaSO_4+SiO_2$ . .	40.7	0.4	4.9	34.8	86.5	99.5
3	$CaSO_4+Na_2SO_4$	58.5	3.0	11.1	18.8	45.1	99.1
4	$CaSO_4+Na_2SO_4$.	41.4	4.2	14.7	47.2	—	—
5	$CaSO_4+NaCl$ . .	52.2	traces	2.3	16.1	69.8	~ 100

The results obtained—influence of catalyzers and additions on the velocity of the reaction studied—having confirmed our suppositions, we also undertook an investigation of the catalytical properties of other catalyzers under the conditions described above, but at a temperature of 900—950° and with mixtures of a stoichiometrical composition $1CaSO_4+0.1$ g-mol. of the catalyzer. An exception was the mixture containing coal, where the ratio was $1CaSO_4+4C$. The values of the SO_3 yield as given in table 2 were obtained as a mean of two reliable experiments.

Table 2

№	Catalyzer added	SO_3 content in initial mixture in %	Yield of SO_3 in % to residue in boat	Notes
1	$NiSO_4$	58.4	70.0	
2	$CuSO_4$	57.9	39.4	
3	$MnCl_2$	53.8	34.6	
4	MnO_2	55.3	34.2	
5	$MgSO_4$	59.4	23.6	
6	Fe_2O_3	54.3	21.3	
7	KCl	55.7	18.5	
8	Charcoal	42.2	1.3	$t°=450—500°$
9	»	42.2	96.2	$t°=700—750°$

The data obtained show that the use of catalysers accelerates the process of chlorination of $CaSO_4$ according to scheme 1. The highest yields were obtained by an addition of $NiSO_4$ (a 12 fold increase) and the lowest by an addition of KCl (a more than threefold increase, if compared with the yield obtained without the use of catalyzers; but, if an allowance is made for the fact that in the absence of chlorine the thermal decomposition of $CaSO_4$ at 900—1 000° falls short of 0.5% the increase will prove even greater).

The part played by the catalyzers, according to our conception, is limited to the evolution of activated chlorine during decomposition of the respective metal (catalyzer) with the succeeding regeneration with the aid of free chlorine.

In the case of chlorination of $CaSO_4+C$ the velocity of the reaction grows considerably because the CaS formed in the first stage of the process, reacts noticeably, according to our observations, with chlorine already at ~200°.

Taking into consideration the temperature measurements at the beginning of the decomposition of $CaSO_4$ and at the beginning of the interaction with SiO_2 that have been obtained by Hoffmann and Mostovitsh (5), Trey (6), Marchal (7), Budnikoff (1) etc., we have come to the conclusion that the acceleration of the reaction according to scheme increases as calcium silicate is formed; the process of formation of the latter is a secondary or ternary process following the dissociation of $CaSO_4$ to CaO or the formation of $CaCl_2$.

The thermochemical calculation of the reaction of chlorination of CaO and the formation of $CaSiO_3$ and also the analysis of the residues for $CaCl_2$ confirm these suppositions.

It follows from the investigations of Tilghmann (8), Budnikoff (1) and others, that the blowing through of steam over heated gypsum increases the yield of SO_3.

Under our conditions, the use of steam could increase the yield of SO_3. Therefore, steam superheated to 150—200° was blown through, in different quantities, together with chlorine, whose admission took place at a rate of 0.1 l/min., over $CaSO_4$, $CaSO_4$+11.4% Na_2SO_4, $CaSO_4$+44.1% SiO_2, $CaSO_4$+10% NaCl heated to 900—950°. It was found that under the conditions described, the use of steam does not increase the yield of sulphur oxides.

Owing to an increased yield of SO_3 due to an addition of Na_2SO_4 to $CaSO_4$ (Table 1), we made experiments for the purpose of studying the influence of different additions of Na_2SO_4 upon $CaSO_4$. In this case we had in view, on the one hand, to utilize the Karabugas sulfate, which is found in immense quantities in the USSR, and, on the other hand, to enrich the issuing gas with SO_2, and, finally, to catalyze the process of decomposition of $CaSO_4$ by the action of the NaCl formed in the process of chlorination of Na_2SO_4. To this purpose, mixtures in stoichiometrical proportions were prepared, where the quantities of Na_2SO_4 corresponding to one grammolecule of $CaSO_4$ varied as follows: 1/16 g-mol. Na_2SO_4, 0.25, 0.5, 1, 2, 4, 8. The experiments were made at 900—950° in the conditions described above. An increase of SO_3 yield was observed with the increase of the amount of Na_2SO_4 in the mixture until the relation Na_2SO_4+2Na_2SO_4 was reached (yield 83.2%). A further increase of the amount of Na_2SO_4 reduced the yield of SO_3 to 60.6%. When chlorinating pure Na_2SO_4, the yield reached 91.4%. On the ground of our observations it may be asserted that in the above conditions at a temperature of 900—950° and with a relation of 1 $CaSO_4$+2Na_2SO_4 the yield must attain 100%, if the mass subjected to chlorination is stirred.

Owing to the interest afforded by the by-product containing $CaSiO_3$, CaO, SiO_2, more detailed experiments were undertaken with a charge containing SiO_2 and $CaSO_4$ in the above conditions, but at 900—950°. To one g-mol. $CaSO_4$ were added 1/16 g-mol. SiO_2,0.25, 0.5, 1, 2, 4, 6, and 8. The yield of SO_3 increased, with the increase of the amount of SiO_2, from 22.7% to 92.1% (the composition being 1$CaSO_4$+ 4SiO_2) then fall somewhat to 90.2% (when the composition was 1$CaSO_4$+6 or 8 SiO_2).

Further experiments were made to study the properties of silica-gel, amorphous silica, rock crystal, crystobalitized Tchasov-Yar sand and fused quartz, mixed with $CaSO_4$ in the stoichiometric ratio 1 : 4, at 900—950°. The investigations were conducted under the above conditions, and in all cases an increased yield of SO_3 as compared with Tchasov-Yar sand was observed. In the case of silica gel and amorphous silica the yield was 99.5%.

A breif steam blast blown over the residue of the 1 $CaSO_4$+4SiO_2 (Tchasov-Yar sand) mixture after chlorination reduces the $CaCl_2$ content to 3.5%, *i. e.* to less than half its value.

In order to study the influence of the duration of chlorination on the accumulation of $CaCl_2$ in the residue left after chlorination, experiments were carried out under the above conditions with a charge $1CaSO_4 + 4\ SiO_2$ (Tchasov-Yar sand), but at 900—950° during 30, 60 and 120 min. In this case a certain increase of $CaCl_2$ (from 8 to 10%) and an increase of the SO_3 yield (98.2% in 120 min.) were observed.

Our further investigations are directed to the utilization of the residue remaining after chlorination of the charge, originally containing SiO_2 and $CaSO_4$, as a cheap activator of basic granulated blast furnace slags with a view to obtain a clinkerless and unburnt cement as an accelerator of hardening of Portland cement and slag cements.

The following conclusions were drawn from the data obtained:

1. The beginning of decomposition of pure $CaSO_4$ by chlorine was observed at 800—850°*t* (or∼800°), and in presence of catalyzers (NaCl, Na_2SO_4, SiO_2, $NiSO_4$, $CuSO_4$, $MnCl_2$, MnO_2, $MgSO_4$, Fe_2O_3 and KCl) at 700—750° (or∼700°).

2. The beginning of decomposition by chlorine of $CaSO_4$ in presence of coal was observed at 450—500° (or∼450°).

3. A simultaneous action of chlorine and steam either on pure $CaSO_4$ or on mixtures of $CaSO_4$ with NaCl, Na_2SO_4 and SiO_2, at 900—950°, failed to increase the yields of sulphur oxides.

4. When using $NiSO_4$ as a catalyzer, the yield of SO_3, in the residue in the boat, at 900—950°, amounted under our conditions to 70.0%; additions of Na_2SO_4 (in the proportion of $1CaSO_4 + 2Na_2SO_4$) gave 83.2%, and additions of SiO_2 gave 92.1% (sand in the proportion of $1CaSO_4 + 4SiO_2$ was used); when using amorphous forms of silica yield of 99.5% was obtained.

5. The velocity of decomposition of $CaSO_4$ with chlorine, in the presence of above named catalyzers and additions, at >600° grows steadily, and the temperature of the beginning of decomposition of $CaSO_4$ falls by 150—350° in comparison with the data of other investigators that have studied the processes of interaction of $CaSO_4$ and SiO_2, but without the simultaneous action of chlorine together with additions or catalyzers.

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CHEMISTRY

BEHAVIOUR OF DIFFERNT MODIFICATIONS OF SILICA TOWARDS CHLORINE AT HIGH TEMPERATURES

By P. P. BUDNIKOV (BUDNIKOFF) and E. I. KREČ (KRETCH)

(Communicated by N. S. Kurnakov, Member of the Academy, 16 IV 1936)

The study of the stability of silica towards chlorine is, in our opinion, of theoretical and considerable practical importance, not only with respect to the selection of materials resistant to chlorine for chemical industry, but also with respect to several other branches of industry, *e. g.* the production of high-grade glass, the use of active pozzualanic additions in Portland cement industry, the production of acid-proof cement, and the ceramic industry.

The action of chlorine on silica has been the object of study for a considerable time. H. Davy (1) and later R. Weber (2), P. Budnikov and E. Šilov (3), R. Wasmuth (4), V. Spicyn (5), W. Fischer and R. Gewehr (6), N. Antonevič (7), and others have studied the reaction of silica with chlorine at high temperatures. Several of the authors have noted the relation existing between temperature, the kind of silica used, the fineness of grind and the rate of the reaction:

$$SiO_2 + 2Cl_2 = SiCl_4 + O_2.$$

The aim of our investigations unlike that of the investigations of other authors, was to study the action of chlorine on different modifications of silica.

Experimental Part

Reagents used; electrolytic chlorine; charcoal; silica-gel obtained from Na_2SiO_3 and screened afterwards (6.2% residue on a 10 000 mesh/cm² screen); amorphous silica obtained as a residue in the analysis of silicates screened through a 10 000 mesh/cm² screen without residue; pure natural rock crystal screened with a 12% residue through a 10 000 mesh/cm² screen; fused quartz obtained from quartz tubes by grinding (9% residue on a 10 000 mesh/cm² screen); Tchasow-Yar sand heated at 600—650° with subsequent grinding (16.5% residue on a 10 000 mesh/m² screen, SiO_2 content 98.5%); cristobalized sand obtained by heating Tchasow-Yar sand at 1550° with subsequent grinding (8.6% residue on a 10 000 mesh/cm² screen).

The treatment of the silica samples under investigation by chlorine was conducted in the apparatus shown in Fig. 1 under the following conditions. If silica was heated before chlorination, the heating continued for 1 hour at the

temperature of chlorination. After this, the boat with silica was cooled, weighed and put into a kiln heated to the temperature needed and filled up by chlorine. In this kiln the silica was subjected to chlorination during 1 hour by an average rate of 0.1 litres of chlorine per minute.

If the sample contained coal, air was blown through it after the chlorination during 15 min. to remove the coal. The mixture with coal was prepared in the stoichiometric ratio 1 SiO_2 : 1 C.

The determination of the percentage of SiO_2 chlorinated was based on the total loss in weight of the boat, the following allowances being made:

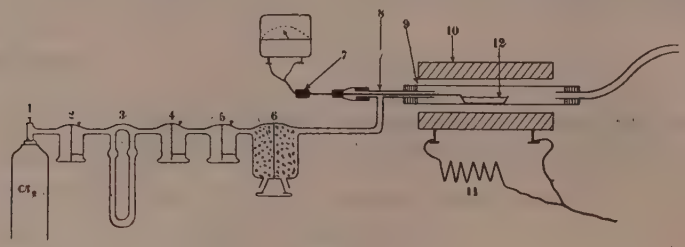

Fig. 1.

1) for the ignition loss of the boat and silica at the corresponding temperature during 1 hour; 2) for the loss due to chlorination of the boat during 1 hour at the corresponding temperature; 3) for the loss due to volatilization of $FeCl_3$, $AlCl_3$, and $CaCl_2$ during the chlorination of cristobalitized and uncristobalitized Tchasow-Yar sand; it was assumed that iron, aluminium, and calcium had been totally removed.

The results of the chlorination of silica-gel and the amorphous silica remaining after the analysis are shown in Table 1. All silica samples were

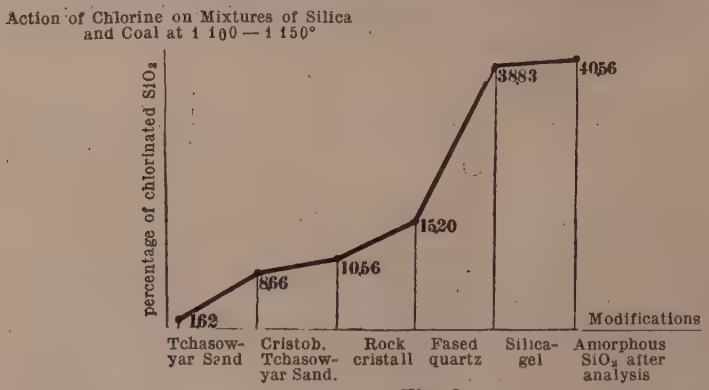

Fig. 2.

burnt before chlorination at the temperature at which the latter was conducted.

The results of the chlorination of rock crystal and of fused quartz are shown in Table 2. The data tabulated below were obtained as a result of chlorination of unburnt samples, owing to the fact that samples burnt at 1 100—1 150° and chlorinated afterwards did not show any loss in weight.

Table 1

Heating and chlorination temperature in °C	Loss in weight after chlorination in percentages			
	Silica-gel before chlorination		Amorphous silica before chlorination	
	Burnt	Unburnt	Burnt	Unburnt
700—750	None	—	None	—
800—850	»	—	»	—
900—950	0.57	—	0.57	—
1 100—1 150	1.46	3.27	1.01	1.30

The results of chlorination of mixtures of different unburnt silica modifications with coal at 1 100—1 150° are shown in Fig. 2 in the form of curves.

In conclusion it should be noted that when treating silica-gel and amorphous silica obtained as a residue after analysis by chlorine, the reaction takes place, not only between silica and chlorine, but partly also between hydrochloric gas forming from constitutional and sorbed water of amor-

Table 2

Chlorination temperature in °C	Loss in weight after chlorination in percentages	
	Rock crystal	Fused quartz
700—750	0.05	0.05
800—850	0.02	0.05
900—950	0.12	0.17
1 100—1 150	0.20	0.25

phous silica and chlorine. When chlorinating modifications other than the basic one, reactions between SiO_2, $SiCl_4$, CO and C also occur.

Conclusions

1. Unburnt rock crystal, fused quartz, burnt silica-gel and amorphous silica obtained as a residue after analysis begin to react with chlorine in porcelain boats at 900—950°C.

2. The addition of coal considerably increases the loss due to chlorination of silica of all the forms investigated.

3. Preliminary burning of silica-gel, amorphous silica, rock crystal, and fused quartz lowers their activity towards the action of chlorine.

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BIOCHEMISTRY

THE AUTOCLAVE SPLITTING OF THE NON-EXTRACTABLE PORTION OF BEEF BY MEANS OF AN AQUEOUS SOLUTION OF LITHIUM CARBONATE

By V. S. SADIKOV and A. G. PESINA

(Communicated by A. Bach, Member of the Academy, 17. VI. 1936)

In using various methods of separating protein from muscular tissue, it is only as an exception that we can extract as much as 50% of the total protein nitrogen of the muscle. Such solvents as water, a 10% solution of NaCl, 5% acetic acid, a 0.225-mole buffer solution of di-potassium phosphate (Howe), or Halliburton's solution (a 0.225-mole solution of $MgSO_4$) extract nothing but globulines and albumines with their concomitant admixtures of nitrogenous and non-nitrogenous extractable substances. The non-extractable fraction of the muscle, which has so far been very inadequately studied, contains 50% of the total nitrogen and is of particular interest in autoclave splitting with a view to obtaining cyclopeptides.

Meat extracted by water, a 10% solution of NaCl, and 5% acetic acid was autoclaved with a 2% water solution of Li_2CO_3. The heating regime was as follows; from 100 to 150°, 23 min; from 150 to 200°, 34 min.; from 200 to 225°, 37 min; at 225°, 10 min. The hot autoclave was removed from the furnace and allowed to cool in the air down to 100°, which took about 90 min. The total duration of heating in the autoclave from 100 to 225° was thus 3 $^1/_4$ hours.

The autoclavolysate had an alcalinity of about 1% and consisted of two phases:

1) a solid residue consisting of a mixture of crystals (lithium phosphate) and resin; the solid phase amounted to 19.15% of the dry substance of the protein taken;

2) a liquid of a light brown colour having colloidal properties. The dry residue of the liquid phase amounted to 72.33% of the dry matter of the non-extractable fraction of the meat. About 9% had been lost in the gaseous phase.

The liquid phase was acidulated with metaphosphoric acid and the lithium phosphate filtered off. The filtrate was then extracted with chloroform in a continuously operated apparatus (for 80 hours). 7.2% of the dry matter of the non-extractable fraction of the meat was taken up by the chloroform.

Solid Phase

An analysis of nitrogen forms in the solid phase (8.4375 g) before and after a repeated open hydrolysis with 25% HCl lasting 36 hours gave the following results:

Table 1

Forms of nitrogen	Before hydrolisis	After hydrolisis
Total nitrogen:		
in grams	0.4823	0.4935
in percentages of dry matter	0.48 (100)	6.63 (100)
Ammonium nitrogen after Folin:		
in grams	0.0448	0.1428
in percentages of dry matter	0.60	1.90
in percentages of total nitrogen	9.28	28.94
Amino-nitrogen after Van Slyke:		
in grams	0.0360	0.2290
in percentages of dry matter	0.04	3.08
in percentages of total nitrogen	(7.64) 6.72*	(46.40) 41.76*
Sum total of ammonium nitrogen and amino-nitrogen in percentages of total nitrogen	16.01	70.70
Residual nitrogen, not determinable by either the Folin or the Van Slyke method	84.00	35.04

Liquid Phase.

An analysis of the liquid phase obtained from 38.83 g of protein and amounting to 28.05 g of dry matter before and after a repeated open hyrolysis with 25% HCl lasting 36 hours gave the following results:

Table 2

Forms of nitrogen	Before hydrolisis	After hydrolisis
Total nitrogen:		
in grams	4.0548	3.9480
in percentages of dry matter	14.45	14.07
Ammonium nitrogen after Folin:		
in grams	0.4282	—
in percentages of dry matter	1.52	—
in percentages of total nitrogen	10.56	3.43 № B*
Amino-nitrogen after Van Slyke:		
in grams	1.3957	2.3023
in percentages of dry matter	4.97	8.21
in percentages of total nitrogen	(43.42) 30.98	(58.59) 52.73
Sum total of ammonium nitrogen and amino-nitrogen in percentages of total nitrogen	41.54	56.16
Residual nitrogen not determinable by either the Folin or the Van Slyke method	58.46	43.84

* After a 10% allowance for the presence of ammonia, determinable by the Van Slyke method as amino-nitrogen.

Residual Phase

An analysis of the liquid phase after it had been extracted with chloroform before and after a repeated open hydrolisis with 25% HCl lasting 36 hours gave the following results:

Table 3

(Dry matter 23.79 g)

Forms of nitrogen	Before hydrolisis	After hydrolisis
Total nitrogen:		
in grams	2.8042	2.8056
in percentages of dry matter	11.78	11.79
Ammonium nitrogen after Folin:		
in grams	0.1299	0.2162
in percentages of dry matter	0.54	0.91
in percentages of total nitrogen	4.38	7.71
Amino-nitrogen after Van Slyke:		
in grams	1.1419	2.0615
in percentages of dry matter	4.80	8.66
in percentages of total nitrogen	(40.71) 36.65	(73.47) 66.12
Sum total of ammonium nitrogen and amino-nitrogen in percentages of total nitrogen	41.03	73.83
Residual nitrogen not determinable by either the Folin or the Van Slyke method	58.97	26.17

Chloroform Phase

An analysis of nitrogen forms in the chloroform extract (dry matter 2.792 g) before and after a repeated open hydrolysis with 25% HCl lasting 36 hours gave the following results:

Table 4

Forms of nitrogen	Before hydrolisis	After hydrolisis
Total nitrogen:		
in grams	0.4973	0.4988
in percentages of dry matter	17.81	17.86
Ammonium nitrogen after Folin:		
in grams	0.0088	0.0523
in percentages of dry matter	0.32	1.87
in percentages of total nitrogen	1.77	10.48
Amino-nitrogen after Van Slyke:		
in grams	0	0.3265
in percentages of dry matter	0	11.69
in percentages of total nitrogen	0	(65.45) 59.90
Sum total of ammonium nitrogen and amino-nitrogen in percentages of total nitrogen	1.77	69.38
Residual nitrogen not determinable by either the Folin or the Van Slyke method	98.23	30.62

Table 5

Comparison of Data Showing the Composition of the Various Phases of the Autoclavolysate

Nitrogen forms in percentages of total nitrogen	Solid phase	Liquid phase	Liquid phase after extraction with chloroform	Chloroform phase
Ammonium nitrogen	9.28	10.56	4.38	1.77
Hydantoin nitrogen	19.66	NB*	3.37	8.71
Amino-acid nitrogen	6.72	30.98	36.65	0
Cyclopeptide nitrogen	35.04	21.75	29.47	58.90
Heterocyclic nitrogen	29.30	33.34	26.17	30.62

From Table 5 the following conclusions may be drawn:

1. The solid phase consists of a mixture of cyclopeptides, di-amino-acids, proline, and heterocyclic substances, amounting in all to 64.34%, the percentage of free amino-acids is low, namely 6.72%. It contains a rather high percentage of ureid or hydantoinic substances, which after open hydrolysis yield free ammonia (19.66%).

2. The sum total of cyclopeptides and heterocyclines in the liquid phase is 55.09%. The percentage of amino-acides is relatively high, namely 30.98%. Ureid complexes occur in negligible quantities.

3. The chloroform phase is characterized by a total absence of amino-acids, a high content of cyclopeptides (58.90%) and hetero-cyclines (30.62%) amounting in all to 89.52% of the total nitrogen contained in the phase. The di-amino-acids and proline are included in this figure. The percentage of ureid nitrogen is 8.71.

The isolation and a detailed investigation of the structure of substances forming part of the solid phase, the chloroform phase and the residual phase of the autoclavolysate of the non-extractable portion of beef are now in progress.

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* After a 36-hour open hydrolisis the liquid phase shows a sharp fall in the ammonium nitrogen content as determined by the Folin method.

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BIOCHEMISTRY

COLLOIDS IN BEETS IN DEPENDENCE ON LIMING OF THE SOIL

By T. T. DEMIDENKO, A. A. KULKES and V. P. POPOV

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The quality of beets as raw material for sugar factories depends to a great extent on the conditions under which the crop is grown. Along with such substances as sugar, the beet may contain a number of harmful admixtures, in particular, the hydrophile colloids, which hinder the process of making sugar. By selecting external conditions of growth, it is possible to obtain beets with various colloid content: the kind of seed, fertilizer, weather conditions—all these have their influence on the formation of colloids in the beet, and not only these, but also the soil conditions under which the beets are grown have considerable influence on the composition and properties of beet juice. Even on one and the same soil variety, under a corresponding change of the cationic part of the soil absorbing complex, the beet reacts to the change by an alteration of its colloido-chemical properties (1).

We attempted to follow out the colloido-chemical changes in the sugar beet if one and the same soil, chernozem, for example, be altered by the introduction of new kations (calcium and magnesium, for example) in increasing doses. This problem is one of great practical interest, since it answers the comparatively little investigated question of how lime fertilization of soil affects sugar beets (5,6).

Considering the fact that a very large percentage of sugar factories are located in the belt of one or another variety of chernozem, which requires the addition of calcium, and that the refuse of sugar factories is itself a source of this calcium, it is apparent that this problem is quite a timely one. It is important to ascertain how the introduction of different kations (for example, calcium and magnesium) affects both the yield and the quality of beets obtained. Under hothouse conditions, we often failed to obtain beets when growing them in sand or in water cultures with the normal nutritive mixtures. It is now known that the beet can develop quite well, if along with other mineral elements boron be continually introduced, even in small quantities. Under these conditions, the beet develops normally and does not rot (2,3,4).

In our investigations, during our study of the colloido-chemical composition of beets grown in lime-fertilized soil, we took into consideration the necessity, along with increasing dose of calcium and magnium and a full mineral fertilizer, of introducing the physiologically important «micro-ele-

Yield and Colloido-chemical Composition

Regime	Yield of roots in grams without micro-elements		Yield in grams with micro-elements		Sugar content
			Roots		
	grams	%	grams	%	
O	85	24.1	85	24.1	14.83
NPK	352	100	352	100	16.62
NPKBFe	—	—	431	122.3	16.74
NPKCaBFe+1/4 h. a. Ca*	386	109.6	427	121.1	16.21
» +1/2 »	375	106.5	414	117.4	15.02
» +1 »	395	112.2	478	135.7	16.43
» +2 »	365	103.7	476	135.0	17.33
» +4 »	348	98.8	449	127.5	17.65
» +6 »	308	87.5	413	117.1	15.95
NPKCaBFe + 1/4 h. a. 75% $CaCl_3$ + +25% $MgCO_3$	290	82.3	308	87.5	16.27
NPKCaBFe +1/2 h. a. 75% $CaCl_3$+ +25% $MgCO_3$	359	101.9	384	109.1	17.67
NPKCaBFe + 1 h. a. 75% $CaCl_3$+ +25% $MgCO_3$	362	102.8	375	106.3	15.95
NPKCaBFe + 2 h. a. 75% $CaCl_3$+ +25% $MgCO_3$	361	102.5	449	127.4	15.21
NPKCaBFe + 4 h. a. 75% $CaCl_3$+ +25% $MgCO_3$	341	96.8	428	121.4	16.01
NPKCaBFe + 6 h. a. 75% $CaCl_3$+ +25% $MgCO_3$	318	90.3	488	138.5	17.44
NPKCaBFe + 1/4 h. a. $CaClO_3$+25% $MgCO_3$	325	92.3	347	98.5	16.80
NPKCaBFe + 1/2 h. a. $CaClO_3$+25% $MgCO_3$	360	102.2	378	107.4	16.80
NPKCaBFe + 1 h. a. $CaClO_3$ + 25% $MgCO_3$	367	104.2	382	108.3	17.62
NPKCaBFe + 2 h. a. $CaClO_3$ + 25% $MgCO_3$	312	88.6	516	146.5	17.15
NPKCaBFe + 4 h. a. $CaClO_3$ + 25% $MgCO_3$	311	85.5	418	118.5	17.12
NPKCaBFe + 6 h. a. $CaClO_3$ + 25% $MgCO_3$	268	76.1	367	104.3	17.12

* h. a.—hydrolytic acidity.

of Sugar Beet with Various Dosages of Lime

Colloids of the leaves			Colloids of the roots		
In grams per 100 cm^3 of diffused juice	Coefficient of amount of colloids	In percentages of dry substance	In grams per 100 cm^3 of diffused juice	Coefficient of amount of colloids	In percentages of dry substances
0.856	33.91	8.6497	0.700	8.67	4.2813
0.738	40.86	9.5301	1.080	8.97	6.9216
0.869	40.07	11.191	0.440	3.77	2.6072
0.600	27.79	7.3434	0.662	5.18	2.6682
1.100	27.78	12.8264	0.350	3.17	1.9834
1.048	38.45	11.9976	1.028	9.50	6.3443
1.471	33.65	16.8957	1.180	10.57	7.2913
1.100	24.90	13.2558	1.338	11.60	8.9934
1.140	39.47	14.6982	1.241	10.75	7.7110
1.020	23.33	11.7063	1.142	10.91	6.9151
0.810	25.08	7.8199	1.121	9.86	6.7310
0.780	27.16	9.8959	1.048	9.52	6.3987
1.257	28.78	12.6042	1.291	12.94	7.9716
1.020	33.67	13.7452	1.500	14.04	10.2590
0.782	21.56	8.6056	1.506	13.50	10.1009
0.683	19.39	6.3798	1.132	9.47	5.5049
1.110	32.28	9.5961	1.170	9.47	5.6837
1.155	26.53	6.6865	1.378	10.24	6.2808
0.839	23.06	6.2123	0.905	7.44	4.3239
0.848	23.31	6.9988	0.987	7.60	4.5727
0.894	18.94	6.8027	1.150	9.28	5.4354

ments»—boron and iron, inasmuch as without these the beet does not develop normally. The data of an analysis of beets grown without the micro-elements have been omitted.

We conducted the experiments in 1935 under vegetative conditions; the soil was the chernozem of the Voronezh Plant Industry Experiment Station fertilized as follows: 1) $(NH_4)_2HPO_4$, 2) KCl, 3) $FeCl_3$, and 4) H_3BO_3. Nitrogen, phosphorus and potassium were introduced at the rate of 1 g of active principle to a pot containing a dry weight of 10 kg of soil; $FeCl_3$—25 mg, and H_3BO_3—15 mg to 1 kg of dry soil. The hydrolytic acidity of the soil was equal to 3.42 milliequivalents.

Date of planting, June 25; of harvest, September 17.

The following conclusions may be drawn from the data on yield and from an analysis of the beets.

1. The curve expressing yield has a general tendency to fall on reaching a maximum height (in the first series with a single dose of lime introduced according to hydrolytic acidity, and in the second series, with a double dose).

2. Magnesium, up to 25% (in the second series), together with calcium, up to the amount of lime taken, in doses from $^1/_4$ to 6 times the hydrolytic acidity, activates the mineral elements and improves the nutrition of the plants. No decrease of yield was observed under the conditions of the experiment despite such large doses of lime as six times the hydrolytic acidity.

3. The role of boron and iron is, undoubtedly, positive, in the sence of tending to increase yield; in the presence of magnesium the micro-elements shift the point of maximum yield to the right, in the direction of large doses of lime.

4. In the presence of boron and iron, the sugar content of the beet steadily increases from 14.83 to 16.84% as the dose of lime increases.

5. On adding magnesium in excess of the dosage as determined according to the hydrolytic acidity, as was the case in our third series of experiments, we observed the maximum sugar content (17.62%) when a single dose of lime was applied, and then, as the dose of lime increased, a gradual, slight decrease in the percentage of sugar.

6. The amount of colloids in beets, which is an important criterion of their quality, must be considered, together with other criteria, in appraising all the measures applicable to sugar beet culture. Liming sharply influences the amount of colloids in sugar beets.

a) The application of boron and iron in addition to NPK fertilizer decreases the amount of colloids in beets.

b) The amount of colloids in the root increases and that in the leaves decreases with an increase of the dose of lime.

c) The minimum amount of colloids in the sugar beet is obtained with half a dose of lime, based on the hydrolytic acidity, while the maximum is reached with a quadruple dose.

d) The application of magnesium increases the content of hydrophile colloids; to avoid excessive accumulation of colloids, it is necessary to use magnesium together with calcium in ratios up to 25% above the calcium norm based on the hydrolytic acidity; thus, a beet with a low colloid content in both roots and leaves is obtained.

7. The introduction of lime into the soil in increasing doses gives a sugar beet with a less viscous juice. In the leaves, increasing doses of lime (Ca+25% Mg) produce an opposite effect, viz., the viscosity of their juice increases (in comparison with NPKBFe).

8. With increase in the viscosity of the juice in the root, surface tension decreases.

9. The use of increasing doses of calcium and magnesium affects both the colloido-chemical composition of the sugar beet and the physico-chemical characteristics of the absorbing complex of the soil, and gives an increased yield if these elements be employed in addition to a fertilizer comprising not only NPK but boron and iron as well.

10. The best components in liming are calcium and magnesium. The latter should be applied at about 25% above the norm for lime based on the hydrolytic acidity. Magnesium, activating the whole plant and soil system, exerts a certain antagonistic action with respect to calcium. As concerns yield, the greatest quantity is obtained with a double dose of lime; while as regards sugar content, even large doses as quadruple or sextuple ones do not produce any negative effect.

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GENETICS

A STUDY OF THE POTATO IN THE GENETIC ASPECT

By A. SCHWARTZ and S. F. KUZMIN

II. VARIABILITY OF PROTEIN CONTENT IN THE *S. PHUREJA*×*S. RYBINII* INTERSPECIFIC HYBRIDS

(*Communicated by N. I. Vavilov, Member of the Academy, 26. III. 1936*)

The possibility of obtaining hybrids and of subsequently evolving therefrom varieties with a high protein content can hardly be questioned.

According to N. N. Ivanov (1), the Illinois Experimental Station, having spent a number of years in breeding forms of Indian corn with high and low protein content, ultimately succeeded in altering the protein content from 10.92 to 16.68% in the case of forms with high protein content, and up to 6.44% in the case of forms with low protein content. W. F. Gerike (2) (according to N. N. Ivanov) regarded the accumulation of protein as an inherited character and held it possible to obtain varieties with an increased protein content.

Pearl and Bartlett (3) showed in their experiments with Indian corn that the content of protein, fat and other substances was inherited in accordance with Mendel's law.

As to the study of the laws governing the inheritance of protein in the potato, this question, as evidenced by the literature available, has so far been but inadequately investigated, so that any contribution to this study can afford a certain amount of interest.

In their previous work (4) the writers, in determining the protein content of some varieties and some hybrids of the potato, observed that the protein content of the potato was, to all appearances, a dominant character, since crossings of a species having a low protein content with one having a high protein content gave in F_1 forms whose protein content approximated very closely that of the parent form with high protein content.

At the same time both F_1 and F_2 showed a wide range of variations of the protein content.

The question arises as to whether these variations in the protein content of F_1 are due the heterozygosity of the parent forms or to individual variability (modification). In their previous work, the writers dealt with average samples of the crop, which made it impossible to trace individual variability. Since every potato plant is the descendant of one tuber, we took, in order to study individual variability, five plants of each hybrid.

Number of *S. phureja* × *S. Rybinii*, viz. Nos.144,145, 149, 155, 156, and, one cultivated variety of *S. tuberosum* Jubel, and determined the protein

content. In order to prevent further fermentation of the raw material, the tubers were cut to pieces and kept for a space of 5—7 minutes in the vapour of a boiling Koch solution. Further drying took place at temperatures not exceeding 50°. The material was then reduced to powder, sifted, thoroughly mixed and sampled for the determination of protein nitrogen by the Barnstein-Stutzer method and for the determination of absolute dry weight (Table 1). The figures shown therein are averages of two determinations in percentages of absolute dry weight. The numbering of the plants (I, II, etc) is arbitrary, the plants being arranged in the order of increasing protein content.

Table 1

Change in Protein Content within *S. phureia*×*S. Rybinii* F_1 Hybrids, Crop 1935 (in percentages of absolutely dry weight)

Name of hybrid or variety	Plant I		Plant II		Plant III		Plant IV		Plant V		Average of 5 plants	
	Protein nitrogen	Protein	Protein nitrogen	Protein	Protein nitrogen	Protein	Protein nitrogen	Protein	Protein nitrogen	Protein	Protein nitrogen	Protein
S. tuberosum (Jubel) . . .	0.78	4.87	0.81	5.06	0.85	5.31	0.93	5.81	0.96	5.99	0.866	5.41
S. phureja× ×*S. Rybinii*												
144	1.19	7.43	1.35	8.44	1.54	9.62	1.54	9.6	1.62	10.10	1.448	9.04
155	1.24	7.75	1.37	8.56	1.49	9.31	1.64	10.25	1.84	11.50	1.516	9.47
149	1.09	6.81	1.17	7.31	1.17	7.31	1.38	8.63	1.46	9.12	1.254	7.83
156	1.14	7.12	1.33	8.31	1.53	9.56	1.66	10.37	1.72	10.75	1.476	9.22
145	1.04	6.50	1.07	6.68	1.16	7.25	1.17	7.31	1.20	7.50	1.128	7.05

In discussing the analytical data, it should be noted that the range of variations of the protein content of the individual plants of the Jubel variety does not exceed 1%, whereas the hybrids show variations as high as 3%.

A comparison of the variations of the protein content within Jubel, a standard variety of *S. tuberosum*, with those observable in one of the hybrid numbers of *S. phureja* × *S. Rybinii* suffices to show that the range of variations between the individual plants of a hybrid number is much wider than that observable in the case of standard varieties.

The range of variations of F_1 clones of the *S. phureja* × *S. Rybnii* hybrids being much wider than that of *S. tuberosum* Jubel variety (Table 1), it is obvious that most clones of the interspecific hybrids *S. phureja* × *S. Rybinii* possess a much higher modifiability than does *S. tuberosum* Jubel.

If the exterme figures of protein content in the *S. phureja* × *S. Rybinii* F_1 hybrids (No 145 has 8.53%, and No 147, 15,68% of protein) are compared with the variations observable between the individual plants of No 156, the most variable of all (plant I having 7.12%, and plant V, 10.75% of protein), it will be seen that the range of variations of the *S. phureja* × *S. Rybinii* F_1 hybrids is much wider than that obtaining within the individual clone of No 156 (Table 2). This is due to the heterozygosity of the parent forms.

In studying the protein content in the potato hybrids, the writers discovered considerable variations of the protein content according to the date of fixation of the material. The hybrids drawn from the 1934 crop and fixed

Table 2

Protein Content in *S. Phureja*×*S. Rybinii* F_1 Hybrids, Crop 1934
(in percentages of absolutely dry weight)

F_1-hybrids	Nos of hybrids . . .	141	142	143	144	145	146
S. phureja× *S. Rybinii*	Protein nitrogen .	1.438	2.130	1.734	2.101	1.365	2.350
	Protein . .	8.98	13.31	10.84	13.15	8.53	14.71
F_1-hybrids	Nos of hybrids . . .	147	149	150	153	154	155
S. phureja× *S. Rybinii*	Protein nitrogen .	2.52	1.685	1.543	1.899	1.626	1.864
	Protein . .	15.68	10.59	9.64	11.87	10.16	11.64

in April 1935 had abundantly sprouted during winter storage in a cellar and showed a much higher protein content than did the same Nos of the 1935 crop. [The fixation of the material took place in Sept. 1935 (Table 3)]. So great a difference may be due, on the one hand, to the influence of soil and climate, and, on the other, to such changes in the bio-chemical composition of the material as may have been traceable to the conditions and the duration of storage. To clear up this point, determinations of the protein content in the same potato hybrids of the 1935 crop were made in December, after a three-months storage in a cellar at a temperature of +5° C; the material in question, having had a brief period of «rest», had sprouted abundantly, which had not been the case with *S. tuberosum* Jubel.

Table 3

Change in Protein Content in Potato as Related to Storage Periods

(in percentages of absolutely dry weight)

Name of hydrids and varieties	September 1935			December 1935			April 1935		
	Total nitrogen	Protein nitrogen	Protein	Total nitrogen	Protein nitrogen	Protein	Total nitrogen	Protein nitrogen	Protein
S. phureja×*S. Rybinii* F_1-hybrids 144 .	1.96	1.448	9.04	2.05	1.631	10.19	—	2.001	13.15
145 .	—	1.228	7.05	—	1.376	8.61	—	—	—
149 .	1.61	1 254	7.83	1.72	1.539	9.62	—	1.685	10.53
155 .	1.97	1.516	9.47	2.17	1.753	10.95	—	1.864	11.64
S. tuberosum Jubel . . .	1.43	0.866	5.41	1.50	0.906	5.66	—	0.724	4.53

A comparison of the data of the three fixations (April, September, December) shows an increase of the amount of total nitrogen and of protein nitrogen due to prolonged storage (Table 3). This apparent increase of the total nitrogen and the protein nitrogen content may be due to the fact that prolonged storage lengthens the period during which there take place in the tuber the processes of respiration and germination, as well the changes of the carbohyd-

rate complex and, consequently, of the whole tuber. The initial content of total nitrogen and of protein nitrogen therefore shows enhanced values, if expressed in terms of the modified complex, while in reality the protein content has changed but little.

In conclusion, we believe to be justified in drawing the following inferences:

1) The genotypes of interspecific hybrids show a greater plasticity in inheriting protein; they show a greater modifiability than do *S. phureja* × *S. Rybinii* and *S. tuberosum* Jubel.

2) In addition to individual variability (modifications) within the clones, we have, in the *S. phureja*×*S. Rybinii* F_1-hybrids a hereditary variability due to the heterozygosity of the parent forms.

3) The apparent increase of the total nitrogen and the protein nitrogen content after prolonged storage of the *S. phureja* ×*S. Rybinii* F_1-hybrids is accounted for by losses in the mass of the tuber, due to the processes of respiration, the sprouting of the tubers, the changes in the carbohydrate complex, which, if expressed in terms of the modified complex, gives a seeming increase of the protein content, while the true protein content would not seem to be greatly altered.

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PLANT PHYSIOLOGY

ON THE PHYSIOLOGICAL CHARACTERISTICS OF YAROVIZED AND NON-YAROVIZED WINTER WHEAT

By I. A. FILIPPENKO

(Communicated by A. A. Richter, Member of the Academy, 9. IV. 1936)

The theory of stage development of seed plants worked out by Academician Lysenko is a powerful resource in the hands of man for controlling the development of plants for his own ends. Along with the important task for practically applying the theory of stage development to the widest possible range of field crops in the shortest possible time, is the extremely important one of studying the physiological processes that occur in plants that have been subjected to yarovization.

The Institute of Plant Physiology began in 1932 to occupy itself with the study of the complicated biochemical processes called forth by yarovization. Academician A. A. Richter and his co-workers A. A. Rancan and M. V. Pekker (1) studied yarovized seed material by working out a biochemical control which would facilitate a characterization of the internal state of the seeds. The authors established the fact that the activity of the fermentative system and the energy of the respiratory process increase in sprouting winterwheat seed under the influence of yarovization. They further discovered a different response of the protein complex in the cells of the growing points of yarovized and non-yarovized wheat seeds to the absorption of basic and acid dyes. Further investigation of the nature of this absorption (2) established a shifting of the isoelectric point of the protein-lipoid complex of the cells of yarovized seed to the acid side.

The biochemical characteristics of jarovized seeds noted above and the profound physico-chemical changes that their protein-lipoid complex undergoes, indicated the desirability of further investigation of the condition of this complex in seedlings and in adult yarovized plants. The response of the water-soluble protein of the leaves of yarovized and non-yarovized plants to high temperatures, their content of the free NH_2 groups and the change in the permeability of the plasm of green leaves were studied. Together with this, a comparative study of the accumulation of dry matter, of the chlorophyll content in leaves, of photosynthesis, and of the activity of the oxidizing ferments was conducted. This last group was taken as an indicator of the vitability of the plants in connection with the fact that the yarovization impulse, greatly hastening development, leads to an increase of grain yield-

1. Method of Investigation

This work was carried out on two winter wheats: Kooperatorka and Lutescens 0329. Yarovized seeds of these wheats were planted in flower-pots in the greenhouse of the Institute. Every five days a new batch of seed was soaked and put for yarovization in the refrigerator at 3 to 5° C. Seed subjected to different periods of yarovization were planted at the same time. In the case of Kooperatorka the yarovization periods were from 5 to 40 days, for Lutescens 0329—from 5 to 55 days.

2. Indices of the Mobility of the Protein Complex

Extracts of the water-soluble proteins were prepared from 4—5 day seedlings of yarovized and non-yarovized wheats. Five grams of seedlings were ground for 5 minutes in a porcelain mortar with 20 cm^3 of distilled water and centrifuged for 5 minutes. The liquids centrifuged off from the yarovized and non-yarovized material were poured into test-tubes, 1 cm^3 to each test-tube, 10 cm^3 of distilled water were added to each, and the test-tubes were set in a water bath, whose temperature was changed by warming and noted down from a thermometer placed in the water.

In Table 1 are given the data on the coagulation temperatures (°C) of the watersoluble proteins of yarovized and non-yarovized seedlings:

Table 1

Variety	Control	Length of yarovization period in days				
		5	25	35	45	55
Kooperatorka	69	67	64	64	64	—
Lutescens 0329	65	64	65	64	62	61

It is apparent from the table that the water-soluble proteins from the leaves of yarovized plants are less thermostable and coagulate more quickly and at comparatively lower temperatures than the proteins of non-yarovized plants. The coagulation temperature of the proteins from incompletely yarovized plants differs little from that of the control, while a sharper difference is noted in plants that have passed through the full period of yarovization. Similar results were obtained in a large number of experiments.

This difference in the rate of coagulation of the proteins indicates a difference in their physical structure. The structure of the proteins was studied from the viewpoint of plasmic permeability. Permeability was determined by the amount of substances that could be washed with water out of the cells of the leaf tissue of yarovized and non-yarovized plants. Determinations were carried out at the early and late phases of the plants development. 1.5 g test portions of the leaves were put in test-tubes, 20 cm^3 of distilled water were poured in, and tubes left for 3—4 hours in a thermostat at 32.5°C. At the expiration of this time, the liquid contained in the test-tubes was poured into flasks, and the quantity of substances that had passed into the water was determined by an interferometer. In Table 2 are shown the absolute readings of the interferometer for pure water and for the extracts.

From Table 2 it is to be seen that the permeability of the plasm of yarovized plants is considerably higher than that of non-yarovized plants. The permeability of yarovized plants rises especially at the time of the onset of the

Table 2

Variety	Interferometer readings			
	Pure water	Non-yarovized plants	Yarovized plants	Remarks
Kooperatorka . .	105	136	213	10-day wheat seedlings
» . .	103	245	287.5	Wheat in tillering stage
» . .	103	332	436.5	Yarovized wheat in stage of stalk formation non-yarovized in tillering stage

stage determining grain formation. These figures indicate a looser structure of the proteins of yarovized plants and, thus, coincide with the data on their temperature stability. The quicker coagulation of the proteins indicates their less stable condition.

M. Ch. Cajlachjan (4) likewise point out the higher permeability of the plasm of spring wheat in comparison with the winter varieties. This fact may show that through yarovization of winter wheat a change in the structure of the proteins is brought about as a result of which this structure becomes typical for spring wheat.

A comparative study of the chemical structure of proteins was carried on by means of determining the free NH_2 groups in the leaves. The determination was carried out in a Van-Slyke test-tube. A test portion of fresh leaves of 0.4 g (second leaves from the top) was grounded in a porcelain mortar, 50 cm^3 of distilled water were added, and the mixture centrifuged. 1.10 cm^3 of the liquid centrifuged off was taken for experiments. These showed that there was considerably more of the free NH_2 groups in the yarovized plants than in the non-yarovized ones. In 10-day seedlings of yarovized Kooperatorka there proved to be 0.9503 mg of amine nitrogen (100), while in 10-day seedlings of non-yarovized plants there were 0.3320 mg (34). In yarovized Kooperatorka in the phase of stalk formation, the quantity of amine nitrogen was 0.0936 mg (100), in the non-yarovized plants 0.0515 (55). In yarovized Kooperatorka in the phase of flowering, there were 0.1603 mg (100), in the non-yarovized, 0.0572 mg (35). These experimental data on the content of the free NH_2 groups indicate the greater chemical mobility of protein substances in yarovized plants in comparison with the non-yarovized ones.

3. Indices Characterizing the General Vitality of Yarovized Plants

A calculation of these indices was carried out both on young plants and those more fully grown. Phenological observations carried out on young plants showed that yarovization produces a marked effect on the external morphological appearance of wheat plants. A sharp difference is to be noted in the differentiation of the young shoots of yarovized and non-yarovized wheat. In the case of yarovized wheat, the first leaf is always shorter and makes a straihgt angle with the second leaf, whereas in non-yarovized wheat, the first leaf makes an acute angle with the second. The same observations were made formerly by A. Serejskij and M. Sludskaja (3). This deflection of the first leaf from the vertical axis is apparently due to a retardation in the growth of

the lower side of the leaf blade. The first leaves of yarovized plants are always coloured a more intense green than the leaves of non-yarovized plants. Quantitative determinations of the chlorophyll content confirmed the difference in colouring that was noted by the eye.

Table 3

Variety and age	Quantity of chlorophyll in percentages										Stage of development
	Control	Length of yarovization period in days									
		5	10	15	20	25	30	35	40	45	
Kooperatorka (10-days seedlings)	32	38	37	34	35	40	40	38	41	—	—
Kooperatorka (38 days) . . .	45	—	31	40	40	45	37	30	40	—	All plants tillering out
Kooperatorka (60 days) . . .	25	—	30	—	32	—	32	39	40	40	To 30 th day, incl., tillering; 40 th day, stalkformation; 45th day earformation

Determination of chlorophyll was conducted on the leaves of non-yarovized plants and those yarovized for different periods—on the 10th, 38th and 60th days after the appearance of the sprouts. Test portions of 0.250 g of fresh leaves were weighed on torsion balance, ground in a porcelain mortar, and the alcohol extract was filtered into a 25 cm^3 flask. The chlorophyll was determined by the spectrocolorimeter of Ljubimenko and Danilov. From the table it is evident that the chlorophyll content in the leaves of yarovized plants is greater than that of the non-yarovized ones. 39 days after sprouting, the content of chlorophyll in yarovized plants decreases, after which an increase in the chlorophyll content is noted, even in plants that were subjected to yarovization for a short period. The quantity of chlorophyll increases sharply at the transition of yarovized plants into the stage of stalkformation and earing. Increased chlorophyll content in yarovized plants coincides with a greater intensity of accumulation in them of dry substance. Thus, the average weight (20 specimens) of a plant of yarovized Kooperatorka after 20 days' vegetation was 17% greater than the average weight (20 specimens) of a plant of non-yarovized wheat. It is characteristic that the young yarovized plants of Kooperatorka lag, in the first period of their growth, behind the young non-yarovized plants. Thus, the average height of 20 specimens of non-yarovized plants after 5 days growth was 9 cm, if yarovized, 5.65 cm. Later the difference in height between yarovized and non-yarovized plants gradually disappears.

The weight of the overground air-dry mass of Kooperatorka which had developed to the stage of ripened grain, was 290% of the weight of non-yarovized plants. The accumulation of dry substance in the leaves was tested by the method of Sachs and confirmed the data cited above with respect to the greater accumulation of dry substance in yarovized plants.

Along with the study of the reducing capacity of the tissues, determinations were made of the activity of the oxidizing ferments, viz. catalase and peroxidase, according to the method of Bach and Oparin. It is found that the activity of the catalase and peroxidase of yarovized Kooperatorka was higher

than that of the ferments of non-yarovized plants. The activity rises especially during the flowering phase, attaining its maximum there, although in the stages of tillering and stalk-formation, it is also considerably higher in yarovized plants than in non-yarovized ones.

N. V. Savostin and M. M. Okuncov (5) carried out determination of the ferments of yarovized spring wheats and also found a more intense activity of the catalase at the time the wheats entered into the stage of ear-formation.

Summing up all the data that we obtained, it is possible to affirm that the yarovization during the course of 35 to 50 days has an enormous influence on the later life activities of winter wheats. This is manifested not only in change of the mode of life, but also in the physico-chemical properties of the plasm proteins complex, which becomes more mobile, and in a higher functional activity of the plants connected with the basic life processes, with photosynthesis and the accumulation of dry substance.

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GEOLOGY

THE «TCHERNIGOV—DONETZ BASIN» VOLCANISM BELT AND THE GEOCHEMICAL PROVINCE CONNECTED WITH IT

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The line of volcanism (1) established by me at points of disjunctive and volcanic significance and at points of gravimetrical anomalies, stretches along the axis of the principal anticlinal of the Donetz Basin (Fig. 1) and continues along the axis of the North Ukrainian syncline (2). It was noted in that paper that the term «belt» of volcanism corresponds more closely to the reality than the term «line» of volcanism and is therefore to be preferred.

Although apparently recognizing the existence of the volcanism line (Luchitski, Sobolev, Svitalskij), some authors confine it to the «Donetz Basin—Isachki» district. Quotations from papers of several authors will help us to make further inferences.

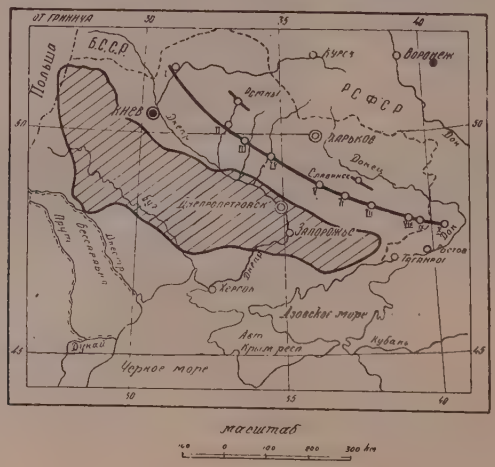
Luchitski (3) notes: «If we draw tectonic lines tentatively traced by Academician Karpinski with additions by Chirvinski and myself and lately by Bezborodko, we obtain, on the whole, one and the same direction running from the region of development of eruptive rocks in the vicinity of Bolshoi Nesvetai, Malyi Nesvetai, Ayuta and Tabunshchikov through Nagolnyi Ridge, Nikitovka and further towards Póltava, near Mirgorod, through Isachki.. and then in the direction of the northern part of Volynia».

We see here a combination of directions formulated by different authors at different periods independently of one other, viz. a) Luchitski (1934): Bolshoi Nesvetai, Malyi Nesvetai, Ayuta, Tabunshchikov.; b) Bezborodko (1931): Nagolnyi Ridge, Nikitovka, Poltava (1933), Mirgorod, Isachki; c) Karpinski-Chirvinski: portion between Isachki and the northern part of Volynia [suggested by Chirvinski (4) in 1928 as an addition to Karpinski's well-known belt].

With regard to a), we must note that the point Tabunshchikov, situated on the prolongation of the axis of the principal anticline of the Donetz Basin (Fig. 1), is to be regarded as pertaining to our line of volcanism, whereas the vein rocks of Ayuta, Bolshoi Nesvetai, Malyi Nesvetai, Tuslov and Kolpakov seem to follow the presumable step-fault of the crystalline belt stretching from the West and overlaid at this place (5) by more recent deposits. This fault marks the beginning of the axis of the crystalline belt,

whose connection with the volcanism line and Karpinski's belt is manifested in the map (6) shown below (Fig. 2).

D. N. Sobolev (7) also rejects the «Isachki-Chernigov» portion, although he admit, similarly to Luchitski, the line of volcanism to be of a tectonic direction. He writes: «Bezborodko has suggested that the (tectonic) line stretches... from Nagolchik as far as Nikitovka and continues further in the North Ukrainian basin, running through Isachki towards the region of the Chernigov anomalies... This original idea deserves to be considered... As



||||||||| Crystalline line the Ukrainian SSR
—o— Line of volcanism
—.—.— External frontiers of the USSR
..... Frontiers of the individual SSR within the Union
I Chernigov
II Isachki
III Mirgorod
IV Poltava
V Lozovaya
VI Ivanovka (near Kramatorskaya)
VII Nikitovka
VIII Alexeyev-Nagolchanski
IX Nagolno-Tarasovskaya
X Tabunshchikov

Fig. 1

to the Chernigov anomaly, the most natural is to connect it with the problem of the boundaries of the North-Ukrainian basin». Further, without modifying the direction of the line of volcanism, Sobolev regards it as «a fault line stretching from the northern border of the Donetz Ridge, may be, across the region of Krasnograd, then across Poltava, south of Mirgorod, towards Lubny (Isachki, N. B.)» (7).

N. I. Svitalski (8) gives a complete scheme of the volcanism line together with its characteristics, adapting it to the metallogeny of the Nagolnyi Ridge.

The doubts expressed by Luchitski and Sobolev as to the tectonic significance of the «Isachki-Chernigov» portion are due not only to a lack of geological data, but also to the fact that both authors interpret the problem of Karpinski's belt as it was originally understood, without any modifications, continuing the belt from Isachki to the Keltci-Sandomir Ridge. The line of volcanism, however, was shown to extend in the direction of Minsk (6). Both the volcanism line and the Ukrainian crystalline belt show that Karpinski's belt should run from Volynia along the Polesski Ridge and further north, as seen in Fig. 2. This figure shows also the separation of Karpinski's belt from the Keltci-Sandomir Ridge.

This doubtful portion stretching between Isachki and Chernigov is borne out by gravimetrical investigation. The gravitation map (Fig. 3) of P. K. Nechiporenko (9)illustrates the accumulation of isolines of gravitation anomalies around Chernigov and Lokhvitsa in the form of concentric ellips-

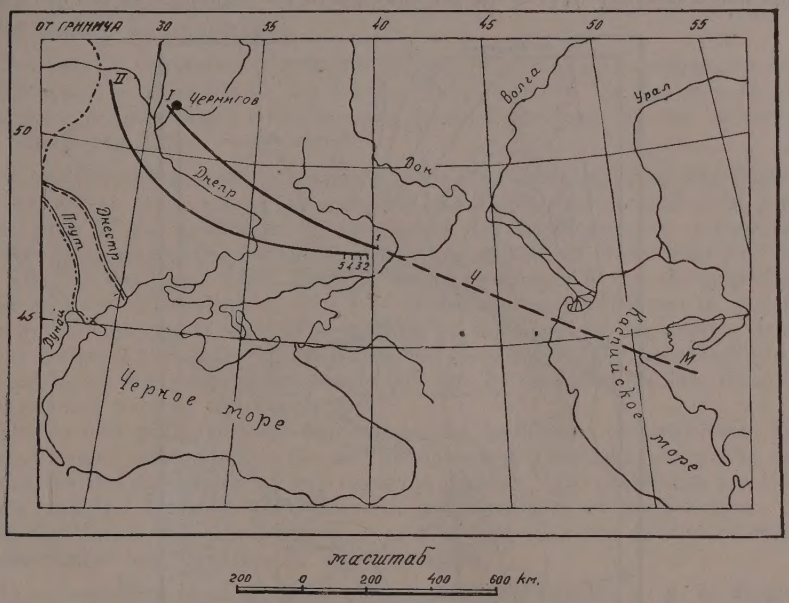


Fig. 2.

I Axis of the crystalline line of the Ukrainian SSR
I «Line of volcanism»
4 Cholon Homur
M Mangyshlak
.. Asegment of the «line of Karpinsky»
1 Tabunshchikov
2 Ayuta
3 Bolshoi and Malyi Nesvetai
4 Tuslov
5 Kolpakov

es. The long axes of the ellipses extend along the line joining Isachki with Chernigov. Nechiporenko concludes that there exists a considerable disjunction along the «Isachki-Chernigov» line and that large masses of igneous rocks of the basalt type occur in the form of laccoliths at two points, viz.: Chernigov and Lokhvitsa. According to the author in question, the laccoliths extend transversely to about 40—60 km (10) to the north-east.

Contrary to the data of Luchitski and Sobolev, the investigations of Nechiporenko corroborate the presence of disjunctive-volcanic processes in the most questionable portion between Isachki and Chernigov. The same investigations reveal the spacial extension of the «line» of volcanism and introduce the term «belt» of volcanism.

The substitution of the term «belt» for «line» is also justified by the presence of vein rocks of the basalt and diabase type in Romny established by the reconnaissance party of the Academy of Sciences of the Ukrainian SSR during the prospecting of the Romny Salt Boss. The tectonics of Romny, judging from the gravimetrical isolines of Subbotin as interpreted by me (12) from the geological point of view in the years 1934—1935, correspond to the WNW azimuth and coincide with the direction of the line «Chernigov—Donetz

Basin». These tectonics are shown in Fig. 1. The distance between Isachki and Romny (70 km) correspods to the width of the belt of volcanims at this place.

Fig. 1 also shows the outcrops of olivine diabase in the vicinity of Slaviansk (Khutor Piatikhatka) ([13]). Its strike, almost meridional and transverse to the basic strikes ([13]), presents an analogy to the tectonics of the ore veins

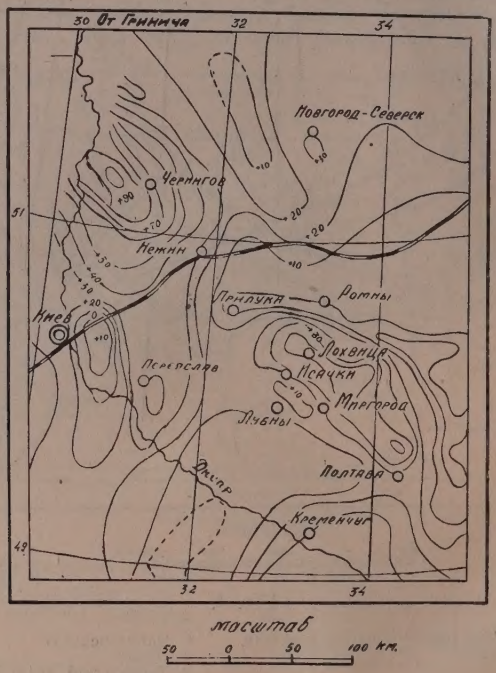


Fig. 3.
Isolines of complete gravitation anomalies ([9])

of Alexeyev-Nagolchanski ([1]). The fact that the occurrence of this olivine diabase coincides with the territory of the volcanism belt point to the deep disjunctions of this belt. The outcropping of magmatic masses in the environs of Slaviansk took place through these disjunctions.

The outcrops of the Romny melaphyre and olivine diabase in the environs of Slaviansk show the spacial extension of the belt of volcanism (Fig. 1).

The «Chernigov—Donetz Basin» volcanism belt affects the geochemical history of a number of chemical elements as well as their occurrence in the form of useful rocks and minerals. Therefore, this belt may be regarded as a definite geochemical province. This province comprises the silver-lead and gold deposits of Nagolchik as well as the mercury ore deposits of Nikitovka. All these ore deposits are encircled in the east (Tabunshchikov), south (Ayuta, Nesvetai, Tuslovo, Kolpakov) and north-west (Slaviansk) by magmatic vein rocks. Considering their mutual genetic connection, new findings of magmatic vein rocks, in still closer proximity to the afore mentioned deposits, should be expected. On the other hand, the possible discovery of new polymetallic veins at other points of the volcanism belt should be regarded as quite natural.

The volcanism belt covers almost completely the copper sandstones of Perm-Carbon. The material of the present deposits seems to have originated from the territory of the same belt.

Valuable radiactive waters, analogous to those of Mirgorod, may be found within the volcanism belt. Reconnoitring with a view to discovering such waters should be undertaken.

The belt of volcanism acquires a special importance in connection with the prospective oil-fields in the Romny Salt Boss (14). The petroleum problem may be connected with the geochemical province of the volcanism belt along two lines.

In the first place such a connection may be established on the basis of the part which tectonics, in general, and the disjunctive tectonics, in particular, play in the process of oil formation. Dynamic pressure is necessary for the decomposition of organic substances and their transformation into oil. Disjunctions and fault fissures serve as channels for the migrations of oil and its concentration. The belt of volcanism enabled me to call the attention of geologists for the first time to the peculiar disjunctive tectonics of the axial part of the North-Ukrainian syncline (1). The possible findings of petroleum are genetically accounted for by the disjunctive structure of the axial part of the syncline.

The second point serving to connect the formation of petroleum with the volcanism belt relates to thermic phenomenon. The most favourable conditions for the conversion of any organic substance into petroleum are those which combine dynamic pressure with a certain rise of temperature. The latter facilitates the polymerization and hydrogenization of non-saturated hydrocarbons and accelerates oil formation.

The association of an oil-field with outcrops of basalts, *e. g.* in Mexico, is usually interpreted as pointing to the processes of disjunction in the lateral rocks favourable to the concentration of petroleum. It should be noted that under conditions of such volcanism, *e. g.* within the territory of the volcanism belt, where huge masses of magma rose to the upper horizon, we are to expect, besides dislocations, a dispersion of considerable supplies of heat accompanied by a rise of the geoisothermal lines of the horizons. in which the formation of petroleum takes place. The rise of geoisothermal lines, as a process favourable to oil formation, may account for the latter in the case of oil fields marked by volcanism.

There is no doubt that seeing the part played by anaerobic bacteria in oil formation (15), we must consider the process of oil formation to be of a mixed type. In the course of such process, owing to an upheaval of large masses of magma into the upper horizons (due to processes of volcanism), conditions of a joint action of pressure and temperature are set up at a certain geological moment.

The interpretation of gravitation anomalies given by Nechiporenko warrants the conclusion to the effect that the mass of magma on the territory of the volcanism belt measures, in some places, many thousands of cubic kilometers.

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